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"NEW ULTRA LOW PERMITTIVITY COMPOSITES FOR
USE IN CERAMIC PACKAGING OF Ga:As INTEGRATED CIRCUITS"

Period August 1, 1984 to July 31, 1987

Final Report

OFFICE OF NAVAL RESEARCH
Contract No. N00014-84-K-0721

DARPA order #5157

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INTRODUCTION

This report documents the work that has been conducted at the Materials Research Laboratory (MRL), The Pennsylvania State University and Interamics in La Jolla, California, for the low permittivity project. This work has been supported by ONR Contract N00014-84-K-0721 under DARPA Order No. 5157. The emphasis was on developing ultralow permittivity (K) substrate materials. Both conventional (evolutionary) and unconventional (revolutionary) approaches were investigated with Penn State and Interamics collaborating. Of the revolutionary approaches, two, namely (a) sol gel and (b) reactive sputter deposited substrates were selected for further development into a viable substrate at Penn State. Currently the emphasis has shifted from development of ultra-low permittivity materials (which has already been achieved) to putting down metallizations on these low K substrates. Thus progress is being made in the direction of a prototype package which would utilize these substrates. This report starts off with the work done on the development of low K substrates and then moves on to the efforts on putting down metal traces and forming vias.

DEVELOPMENT OF LOW K SUBSTRATE MATERIALS

(A) CEMENTITIOUS ROUTES

(1) Macro-defect-free calcium aluminate cements

The work in this area has been conducted by Paul Sliva (graduate student) with guidance from Drs. L. E. Cross, D. M. Roy and B. E. Sheetz.

MACRO-DEFECT-FREE CALCIUM ALUMINATE CEMENTS

Work in the development of calcium aluminate cement as a low relative dielectric permittivity substrate is focused on primarily three topics:

1. Processing analysis of thin cast tapes including: a complete milling study, non-aqueous casting of thin tapes via doctor blading, a sintering study and sintered laminate characterization.
2. A continuing characterization of shear-mixed cements keying on thermal conductivity and an extensive investigation of the dielectric response and loss tangent at microwave and far infrared frequencies.
3. A study of the binding mechanisms between poly (vinyl alcohol) macromolecules and calcium and aluminate ionic species.

Tape Casting

A brief overview of the work will be presented here. Further details are included in Appendix 1.

Secar 71 cement was vibratory milled for 48 hours in 95% ethanol using zirconia media to define milling parameters for surface area, pit, viscosity, particle size distribution and zirconia contamination. Several sample batches were cast using an acetate-based binder system* (Table I). A solids loading of 20 vol% (42.5 wt.%) provided tape of the highest green density (1.66 g/cc). Average tape thickness was $76 \pm 0.90 \mu\text{m}$. Samples were heated using a burnout schedule from 25°C to 600°C. Laminates were prepared as a stack of 12 tapes. A series of firing temperatures indicated that the highest density (2.66 g/cc) and greatest shrinkage (18% linear) occurred at 1450°C in air (Table II). Figure 1 is a flow chart describing the various steps to produce sintered laminates.

The dielectric constant and loss tangent were measured over a wide frequency range. Figure 2 shows the response of the dielectric constant and loss tangent at low frequencies. The dielectric constant ranges from 10.9 to 10.7 and the loss tangent from 0.006 to 0.003. Using a post resonance technique in the microwave region at 18.45 GHz, the dielectric constant and loss tangent were 5.5 and 0.003, respectively. From Fourier Transform Infrared Spectroscopy, spectral reflectance data near $3 \times 10^{12} \text{Hz}$ indicates the presence of an intense oscillator that raises the dielectric constant to ~ 130 . At higher frequencies, the dielectric constant assumes a stable value near 9. Noise from the scans was too high to obtain a Kramers-Kronig analysis necessary to obtain both the real and imaginary parts of the dielectric constant.

The dielectric constant and loss tangent as a function of temperature were determined at a frequency of 1KHz for 4 electroded samples. The results are shown in Figure 3. The temperature coefficient of capacitance appears to be quite reproducible and has a mean value of $+120 \pm 15 \text{ ppm/}^\circ\text{C}$. There is little apparent change in loss with temperature.

Volume DC resistivity taken at room temperature and 100V averaged $1.6 \times 10^{15} \text{ ohm-cm}$. Average thermal conductivity at room temperature was 2.54 W/m-K. A compilation of fired substrate properties is given in Table III.

Microstructural observations were made using a scanning electron microscope. An unpolished surface (Figure 4) indicates that the grain size is probably in the 2 - $5 \mu\text{m}$ range. Fracture micrographs in the plane perpendicular to the laminations (Figures 5a and b) show nearly complete transgranular fracture, an indication of no weak grain boundaries. Much of the porosity was very fine ($<1 \mu\text{m}$) with a lesser incidence of large (2-3 μm) regularly shaped pores.

TABLE I
Composition of Tape Casting Test Batches.

Batch No.	Weight % SECAR 71	Volume % SECAR71	Volume % Binder*
1	9.18	3.62	96.38
2	28.04	12.65	87.35
3	38.70	19.00	81.00
4	44.56	23.00	77.00
5	49.88	27.00	73.00
6	54.73	31.00	69.00

* Metaramic Sciences, Carlesbad, CA; Type CB73140
(binder density ~1.1 g/cc)

TABLE II
Firing Temperatures, Densities and Percent Transverse Shrinkage of Sintered Calcium Aluminate Cement Laminates.

Firing Temperature (°C)	Average Density (g/cc)*	% Transverse Shrinkage
1200	1.68 ± 0.02	9
1250	1.64 ± 0.03	9
1300	1.66 ± 0.05	11
1350	1.89 ± 0.02	14
1400	2.10 ± 0.01	18
1450	2.66 ± 0.01	18
1500	2.45 ± 0.01	16

* Average of four geometrical densities

PROCESSING FLOW CHART

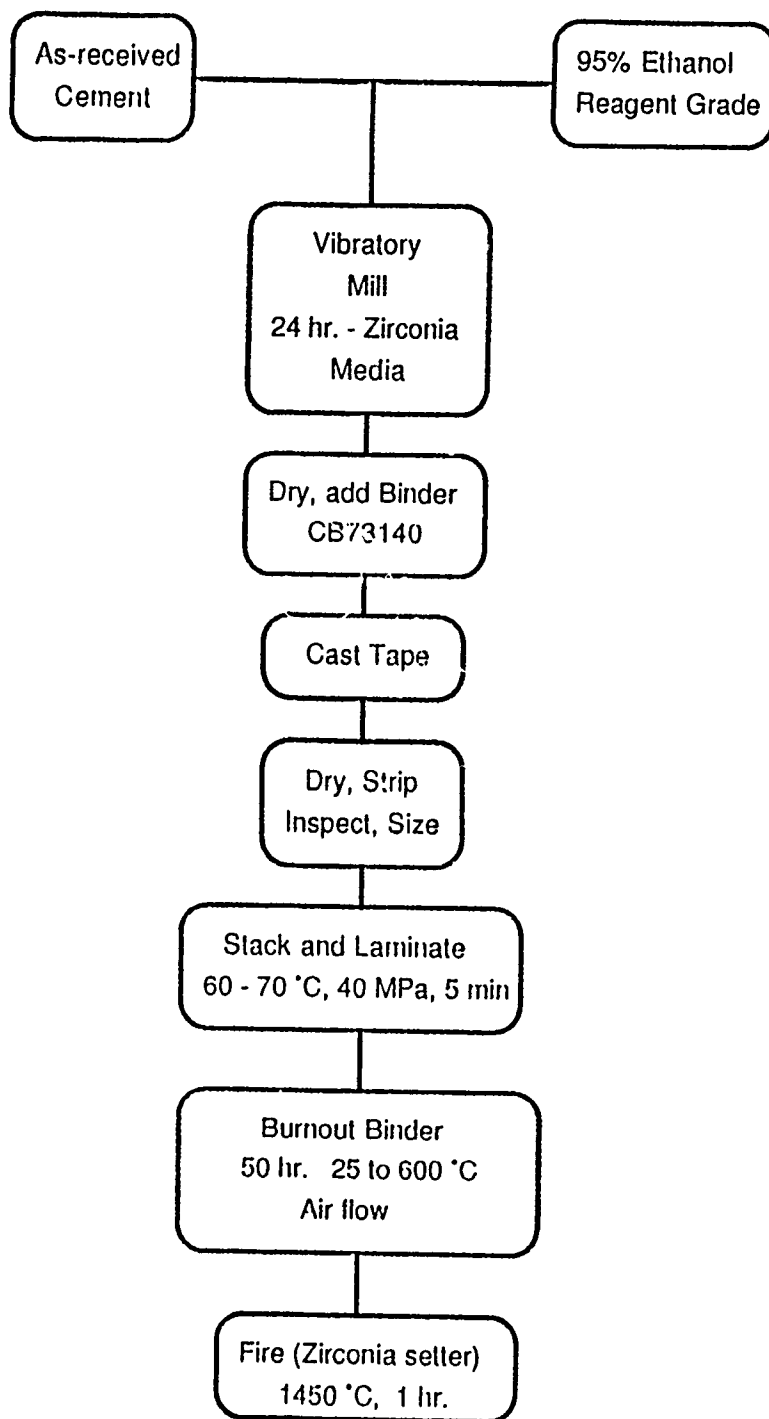


Figure 1 Processing Flow Charter Describing the Steps to Produce Sintered Laminates.

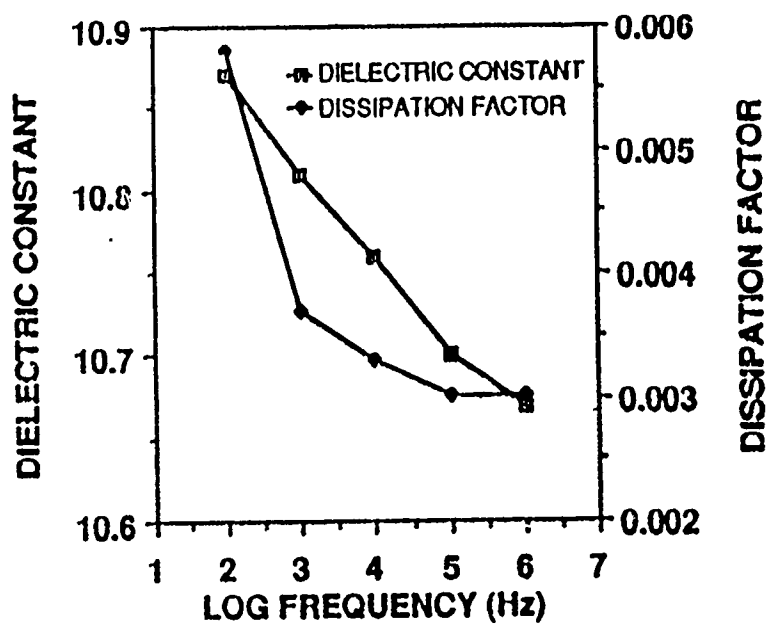


Figure 2 Mean dielectric constant and loss as a function of frequency from 100 Hz to 1 MHz for SECAR 71 substrates fired at 1450°C for 60 minutes.

TABLE III

Fired Substrate Properties

Sintered Temperature (°C)	1450
Sintering Time (min)	60
Fired Density	2.66
Transverse Shrinkage (%)	18

Room Temperature Dielectric Constant/tan δ

1.0×10^3 Hz	10.8/0.004
1.0×10^6	10.7/0.003
1.0×10^9	5.5/0.003
$>3.0 \times 10^{12}$	~ 9 / -----
Temperature Coefficient of Capacitance (ppm/°C)	120 ± 15
D.C. Resistivity (@ 22 ± 1 °C)	1.6×10^{15}
Thermal Conductivity (w/m-K)	2.54

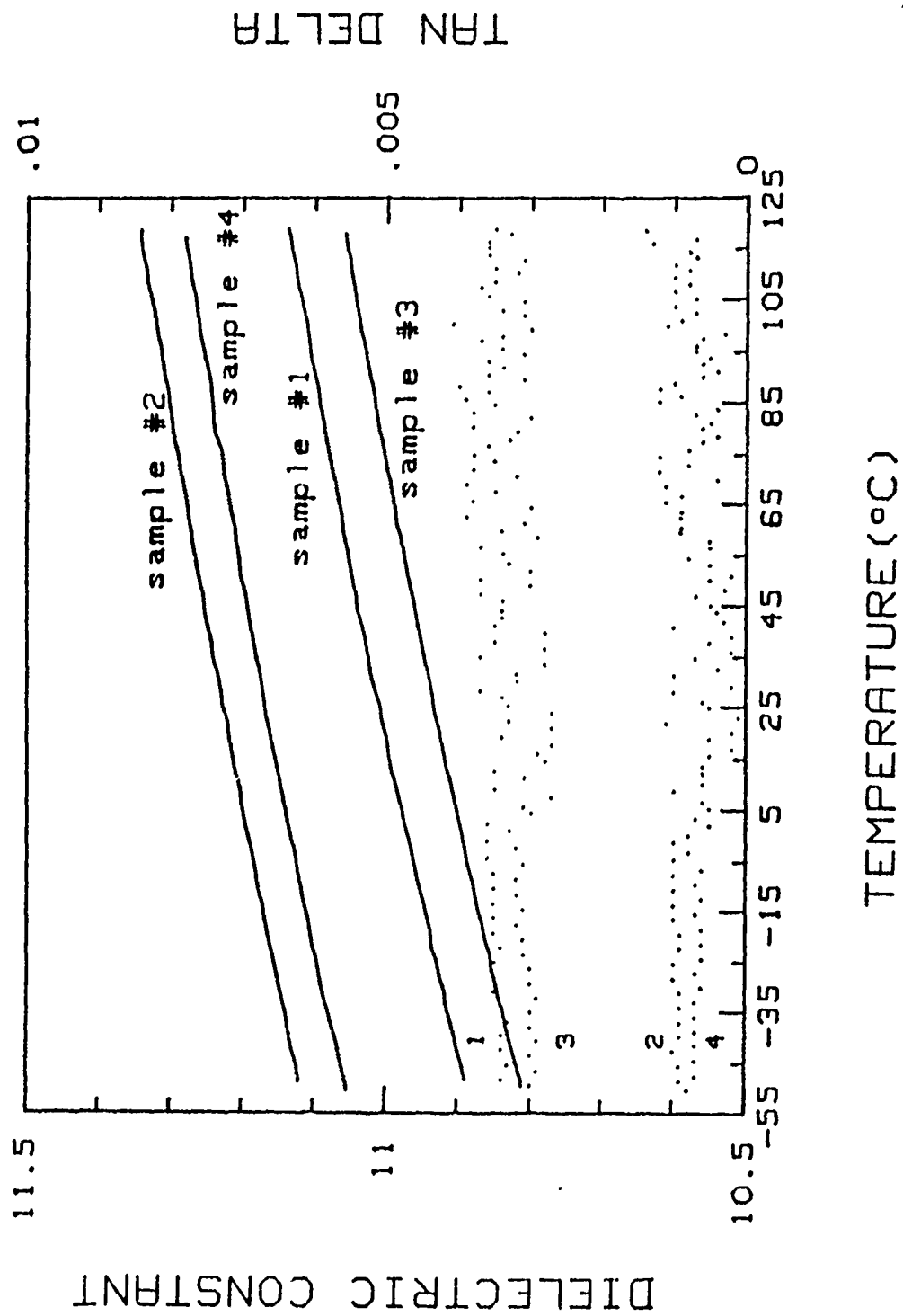


Figure 3. Dielectric constant and loss as a function of temperature for SECAR 71 substrates fired at 1450° C for 60 minutes.

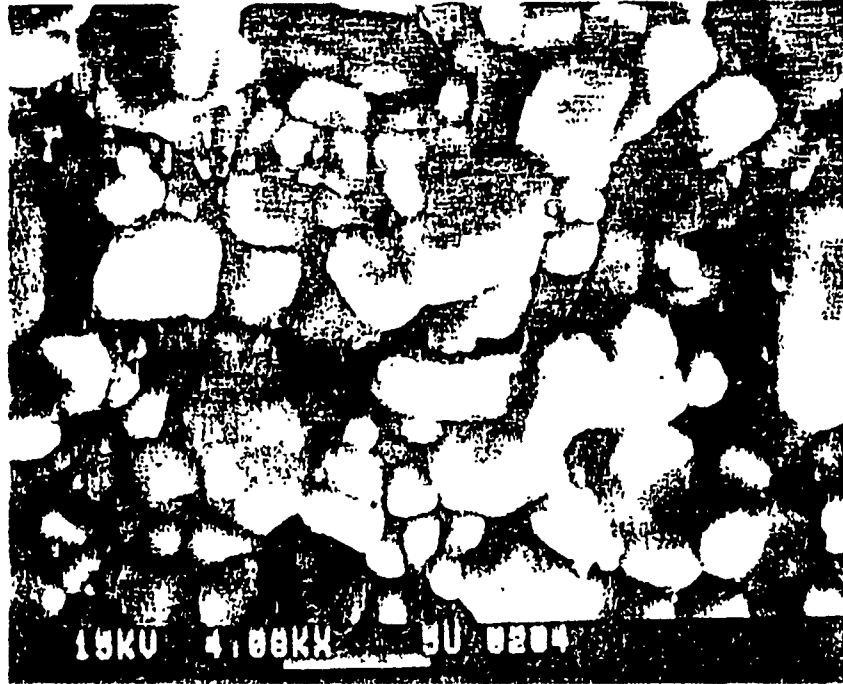
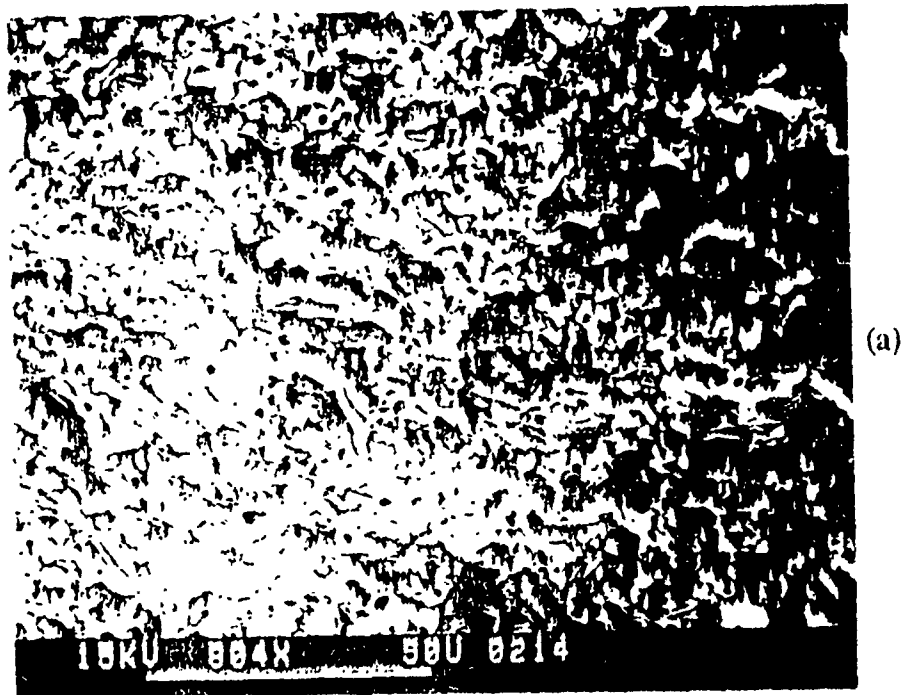


Figure 4 As fired surface of SECAR 71 laminate fired at 1475°C for 60 minutes (~4000x).



(a)



(b)

Figure 5 Fracture surface perpendicular to layers of SECAR 71 laminated substrate fired at 1475°C for 60 minutes: a) ~800 x; b)~4000x.

Shear Mixed Cements

Microwave Frequency Measurements of K , $\tan \delta$

An investigation of the dielectric response of shear mixed cements at several frequencies in the microwave region is investigated. Measurements have been made at only one frequency, $\sim 10\text{GHz}$. Three different cements, SECARS 60, 71 and 80 were investigated, although SECAR 71 was the targeted cement for substrate applications. Studying all three cements will help discern differences in the dielectric response as a function of cement composition.

Samples were prepared using a standard shear mix procedure that was developed and documented in several previous reports. The procedure consists of mixing the cement with a 10.0 wt.% poly (vinyl alcohol) (PVA) solution (low M.W., $\sim 80\%$ hydrolyzed) and mixing under vacuum A C.W. Brabender preparation mill. The batch has a water/cement of 0.20 and contains ~ 1.8 wt.% PVA. The resultant plastic cement paste is weighed out and uniaxially pressed into disks of $1.905\text{cm } \phi$ (0.75 inch ϕ) and vary lengths between 0.9 and 0.4 cm. The pressure cycle is repeated three times to ensure the escape of any trapped air in the sample. The disks were removed from the die, dried in air overnight and stored over overnight. Before making measurements, the samples were slowly heated to $\sim 110^\circ\text{C}$ overnight to remove residual moisture.

Microwave measurements were made using a post resonance technique. The sample is placed between two large conducting plates. A swept signal induces a resonance in the sample from which the dielectric constant and loss tangent can be obtained. Four samples of each cement were measured. Table IV shows average values of dielectric constant and loss tangent for disks made of the three different cements.

SECAR 80 resulted in the highest dielectric constant due to the α -alumina present. SECAR 71, the target cement, had the lowest dielectric constant. All three cements had similar losses.

Thermal Conductivity

All of the five different SECAR cements were tested for thermal conductivity. Samples were again prepared by the shear mixing process described previously. Disks were pressed to 20,000 psi and had dimensions of $\sim 5.08\text{ cm } \phi$ (2 inches ϕ) by ~ 1 cm thick. One sample disk of each cement was made. The curing procedure was to dry in air and store over drierite. The disks were not heated before measurement and therefore contained absorbed water. Samples were ground and polished to $1\text{ }\mu\text{m}$ fineness.

The technique used for the measurements is an in-house technique where a heated thermocouple is brought into contact with the sample being kept at room temperature. When contact is made the EMF rises rapidly to a steady state value. The measured EMF is proportional

TABLE IV

**Average Values of Dielectric Constant and Loss Tangent for
SECARs 60, 71 and 80 Measured at ~10 GHz.**

<u>Cement</u>	<u>Dielectric Constant</u>	<u>Loss Tangent</u>
SECAR 60	5.09 ± 0.17	0.0051 ± 0.002
SECAR 71	4.64 ± 0.36	0.0060 ± 0.0002
SECAR 80	6.51 ± 0.12	0.0070 ± 0.0009

TABLE V

Thermal Conductivity of Shear Mixed Calcium Aluminate Cements

<u>Cement</u>	<u>Density (g/cc)</u>	<u>Thermal Conductivity (W/m-K)</u>
SECAR 60	2.09	1.70 ± 0.04
SECAR 71	1.85	1.03 ± 0.06
SECAR 80	2.26	1.93 ± 0.14
SECAR 80 fast set	2.23	1.94 ± 0.12
SECAR 80 Modified	2.28	1.83 ± 0.09

to the square root of the thermal conductivity. A series of standards are used for calibration. Several measurements were taken to assure reproducibility.

Table V gives the average values of the thermal conductivity for the different cements. As expected for cements, they all are of low thermal conductivity. The cements containing α -alumina, SECARS 80, 80 fast set and 80 modified, all exhibit a high thermal conductivity. SECAR 60 contains SiO_2 which helps raise the conductance. The sample made of SECAR 71, although about as dense as the others, gave a relatively low value of thermal conductivity. SECAR 71 does not contain any α -alumina or SiO_2 .

Poly (Vinyl Alcohol) Macromolecule Binding Mechanisms

This work was started rather late in the program. Therefore, only background and preliminary results will be discussed.

When calcium aluminate cement is mixed with poly (vinyl alcohol) (PVA), it has been proposed by the work at Imperial Chemical Industries that the calcium and/or aluminum ions crosslink the polymer to form a bond and develop strength rather than through hydration. However, the extent of the crosslinking and which of the ionic species are involved is still uncertain. Consequently, this study was undertaken in order to better understand the mechanisms of strength development and the response of the dielectric properties of cured, shear mixed cement.

Preliminary experiments to date of shear mixed cements show that when SECAR 71 is mixed with PVA, the PVA becomes exclusively rich in aluminum. Figures 6 and 7 show the EDX chemical analysis of as received PVA and PVA that has been mixed and cured with SECAR 71 cements, respectively. In the as-received PVA, only the gold peaks are present from the conductive coating. However after curing with SECAR 71 cement, aluminum is obviously present, but no calcium (along with the gold).

The binding constants of calcium and aluminum with PVA are being determined by solution chemistry. Inferences of the results will be referred back to the system SECAR 71-water-PVA. The sample matrix includes: varying the PVA and ionic species concentration, using three different PVA molecular weights (from ~40,000 to 140,000) and varying the pH.

The experimentation involves mixing aluminum and calcium (separately) in the form of soluble nitrates with PVA solution and titrating with a base, tetra-ethyl ammonium hydroxide. Variations in the titration curves along with specific conductance measurements will be used to determine the extent, if any, of binding by the ionic species. From this, the binding constants for calcium and aluminum with PVA can be calculated.

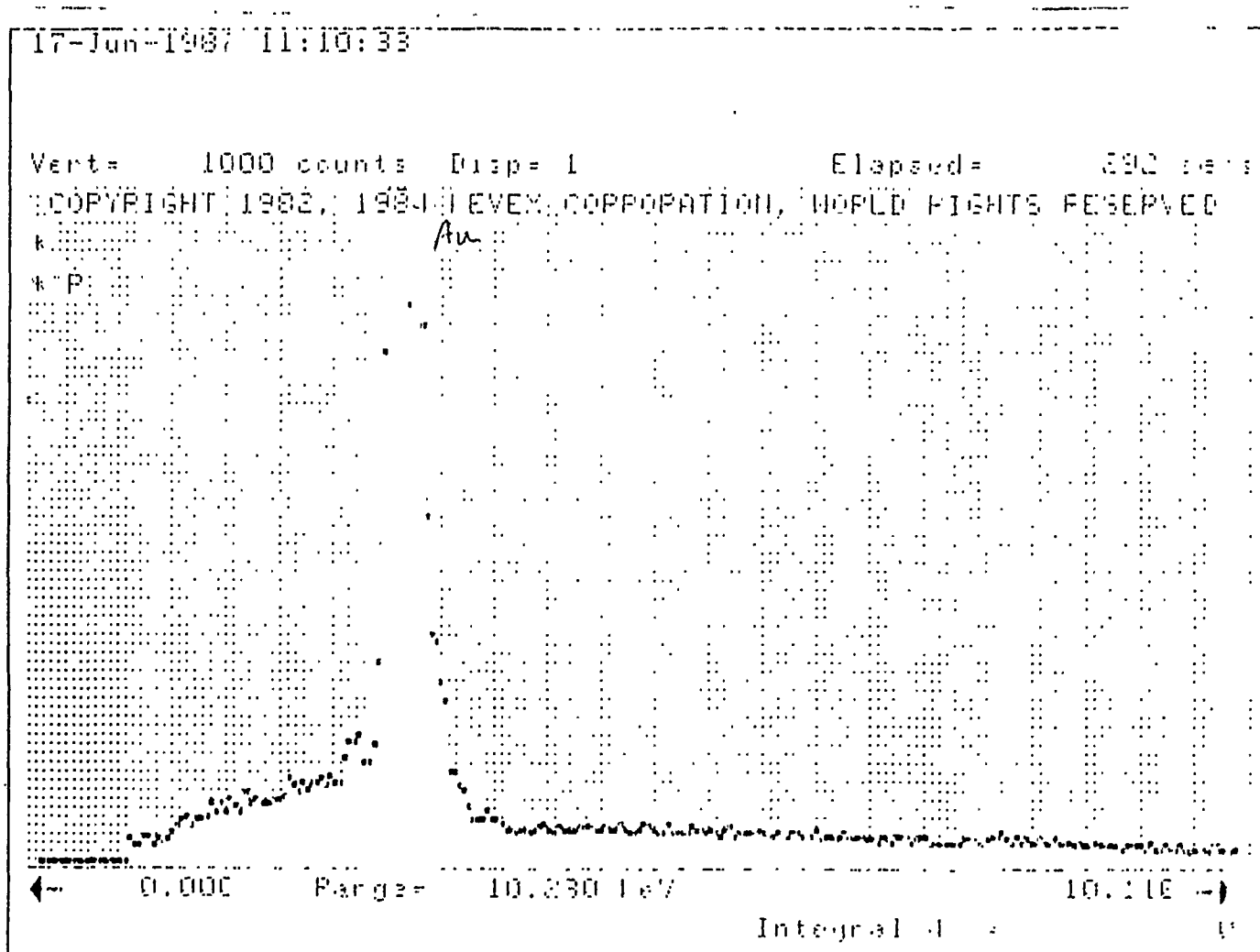


Figure 6 Energy Dispersive X-Ray Analysis of As-Received Poly (Vinyl Alcohol)

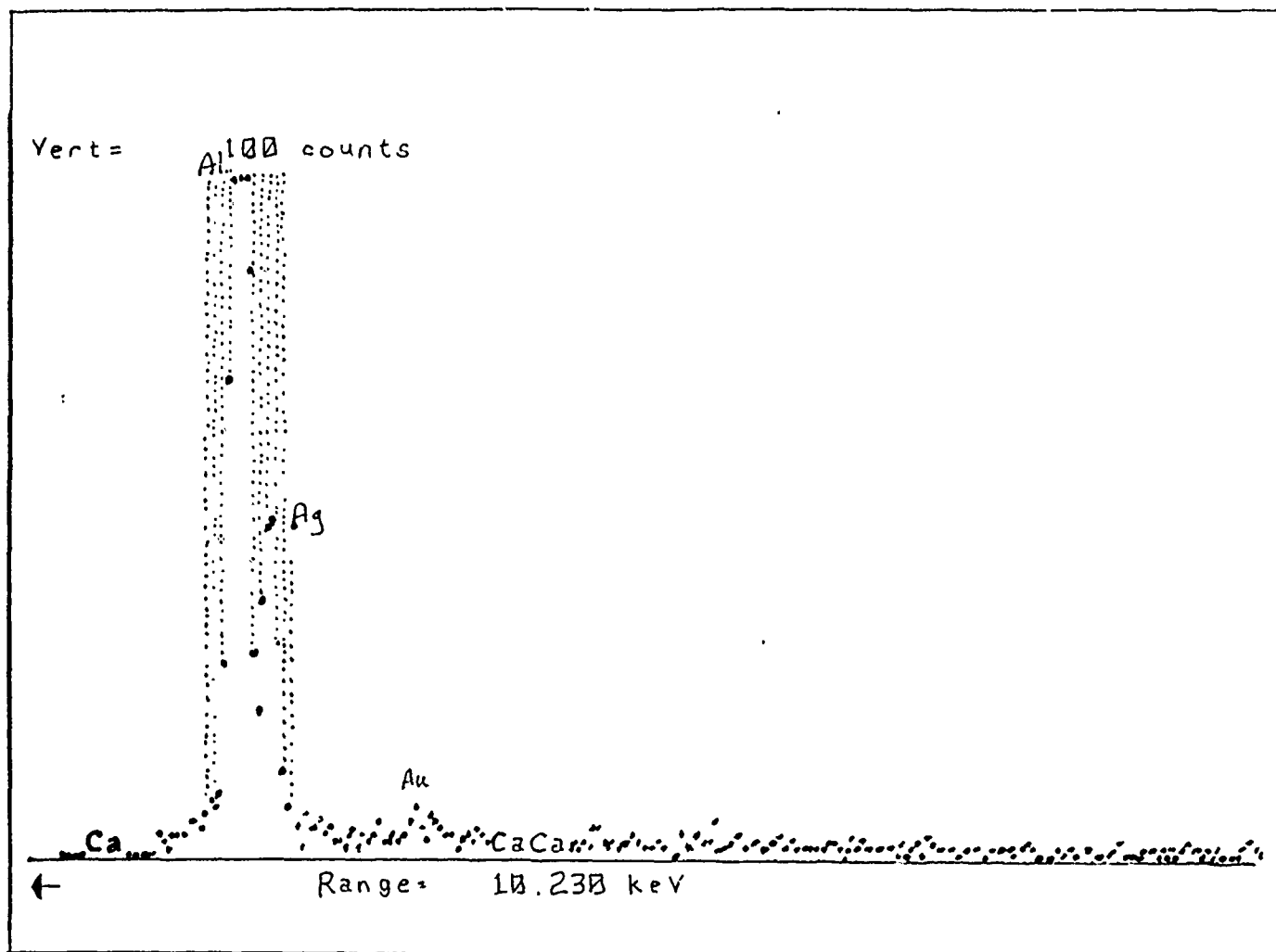


Figure 7 Energy Dispersive X-Ray Analysis of Poly (Vinyl Alcohol) after Mixing and Curing with SECAR 71 Calcium Aluminate Cement.

Tape Casting

A logical step for the formation of sintered laminates is to add glass microspheres to lower the dielectric constant. The softer processing (compared to shear mixing) should result in a high survival rate of the microspheres. For SECAR 71, a 20 or 30 vol.% addition of hollow silica microspheres will lower the dielectric constant to 3.3 and 2.9, respectively.

Further characterization of the sintered laminates and pressed bodies should be conducted, including: dielectric constant and loss tangent over a wider range of microwave frequencies, mechanical properties and moisture sensitivity.

An exploratory study should be performed on the back hydration of partially sintered laminates to take advantage of the three-dimensional porosity to develop strength but retain the porous microstructure.

PVA Macromolecule/Calcium-Aluminum Binding

The determination of the binding constants for calcium and aluminum with PVA is important. The study by IR and Raman spectroscopy should be done to ascertain the interaction of the PVA with calcium aluminate cement.

C3S and Slag with Silica Composites

This study has been conducted by Dr. M. Perez with guidance from Dr. D. M. Roy. The work can be divided into two parts. The first part refers to Figure A(2).1. The Cab-O-Sil (10 and 20 wt.%) and C3S slurries were prepared by the following procedure. First, the Cab-O-Sil was added to deionized water at a solid content of 13 wt.% and stirred. Simultaneously the C3S powder was added separately to deionized water at a solid content of 27 wt.% and stirred. After 30 minutes and while still stirring the C3S suspension the Cab-O-Sil solution was added to it. The resulting slurry was further stirred for 30 minutes; then, simultaneously heated and stirred until stirring was not possible because of the increase in solids concentration due to the water evaporation. The resulting paste was further dried at 100°C until the total solids content increased

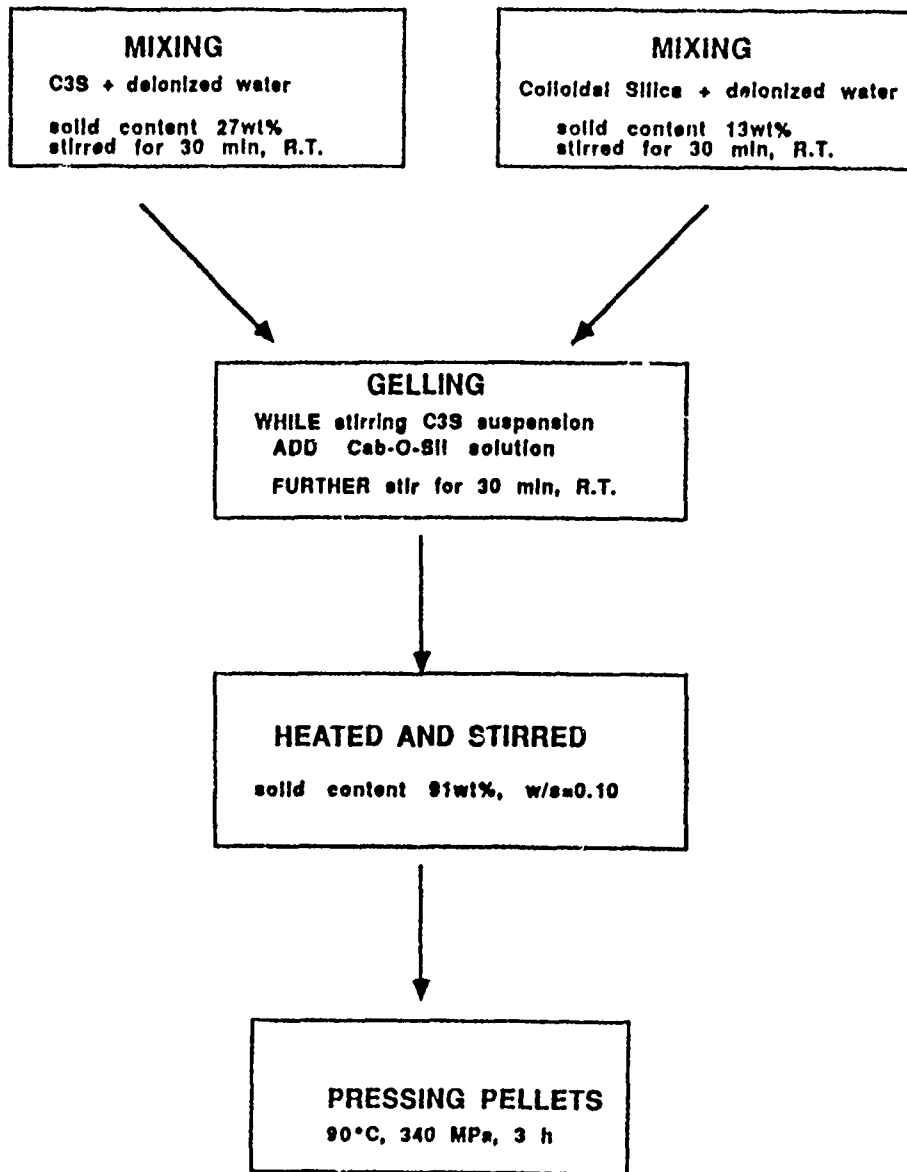


Figure A(2).1 Processing of Amorphous $\text{SiO}_2/\text{Cu}_3\text{Si})_5(\text{C}_3\text{S})$ Composites.

to about 91 wt.%, i.e. a water to solid ratio (w/s) of 0.10. The total drying period takes approximately 3.5 h. A homogeneous powder was observed when examined under a low magnification optical microscope.

The dried mixture was placed into a stainless steel die and then loaded into a press with temperature set at 90°C. The pressure used of 340 MPa was released after 3h, and samples were cured at 90°C overnight inside the die.

The dielectric permittivity and losses were measured by placing the samples inside and waveguide as shown in Figure A(2).2. The frequency range was between 8×10^9 to 1.3×10^9 . The dielectric permittivity as found to be around 5. With 20% Cab-O-Sil the permittivity was slightly lower. The losses were less than 5% (refer to figures A(2).3(a) and A(2).3(b)). The scattered nature of the losses is probably due to instrument noise.

The second part of this study uses slag cement (MC 500) and Cab-O-Sil, which are sintered to form Mellilite/Wollastonite substrates. The samples were prepared according to the flow chart in Figure A(2).4. The powders (80 wt.% MC500 and 20 wt.% Cab-O-Sil) were milled in ethanol using Al_2O_3 grinding balls in polyethylene containers. The slurries were dried in air at 90°C. Samples were preceeded at 340 MPa, then fired in air at 800 and 900°C for six hours at a heating rate of (a) 3.5 and (b) 10°C/min. It should be mentioned that after drying no binder was necessary and because of the high surface area of the dry powder it was relatively easy to for the samples by dry pressing.

The dielectric permittivity was measured using the same technique mentioned before. The permittivity of the samples sintered at 800 and 900°C with 20% and 10% Cab-O-Sil are shown in Figure A(2).5. The losses were similar to those shown in the first part.

The advantages of these two different processes is that they are relatively inexpensive and the sintering temperatures are lower than that of conventional alumina substrates.

(B) SILICA, HOLLOW GLASS MICROSPHERE 0-3 COMPOSITES

This investigation, using hollow glass microsphere (HGMs) with a lead glass frit (0-3 composite) was conducted by Marcia Leap (graduate student) with the guidance of Dr. W. Huebner (Asst. Professor of Ceramic Science, Penn State).

B.1 Powder Characterization

HGM composites were fabricated from silica hollow glass microspheres (Emerson and Cuming's Eccospheres SI) and a ground lead glass frit obtained from O'Hommel. Both powders were studied using x-ray diffraction and spectrochemical techniques to test for crystallinity and to

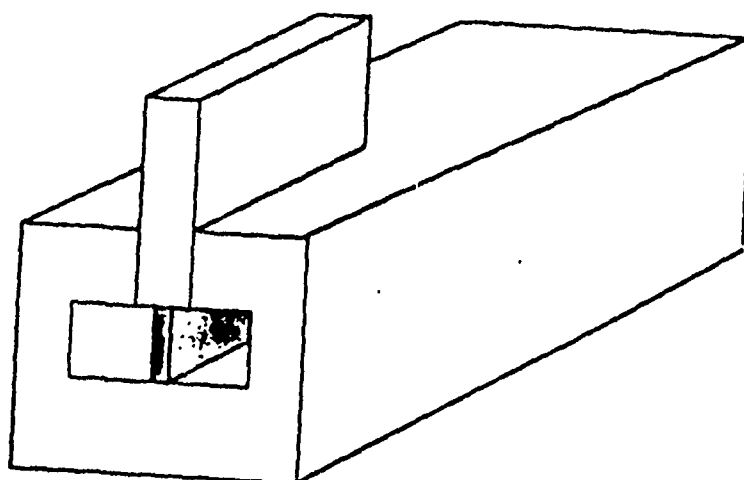
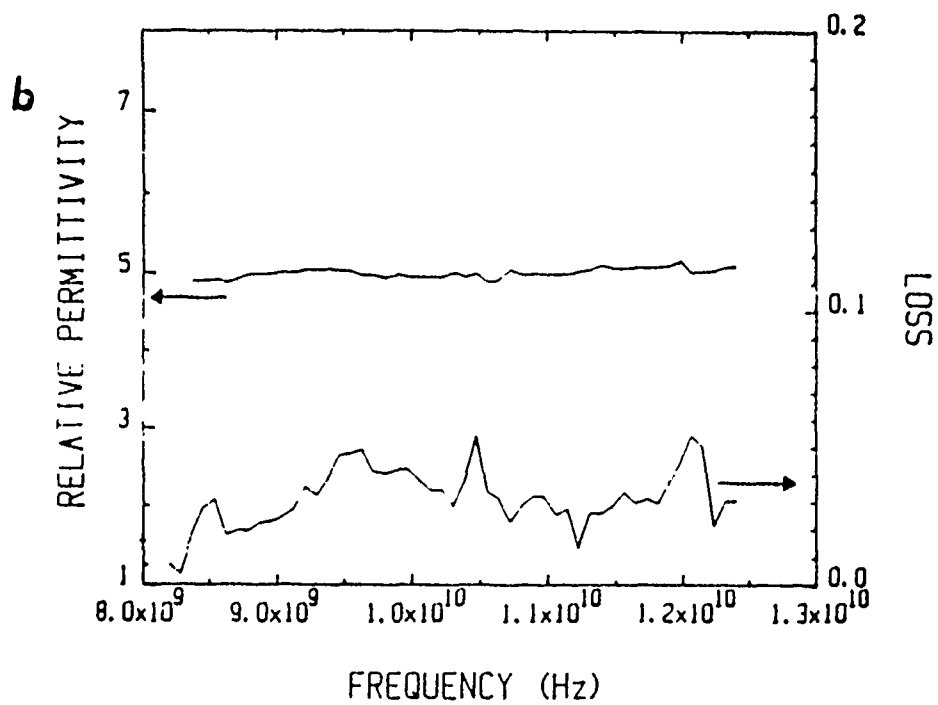
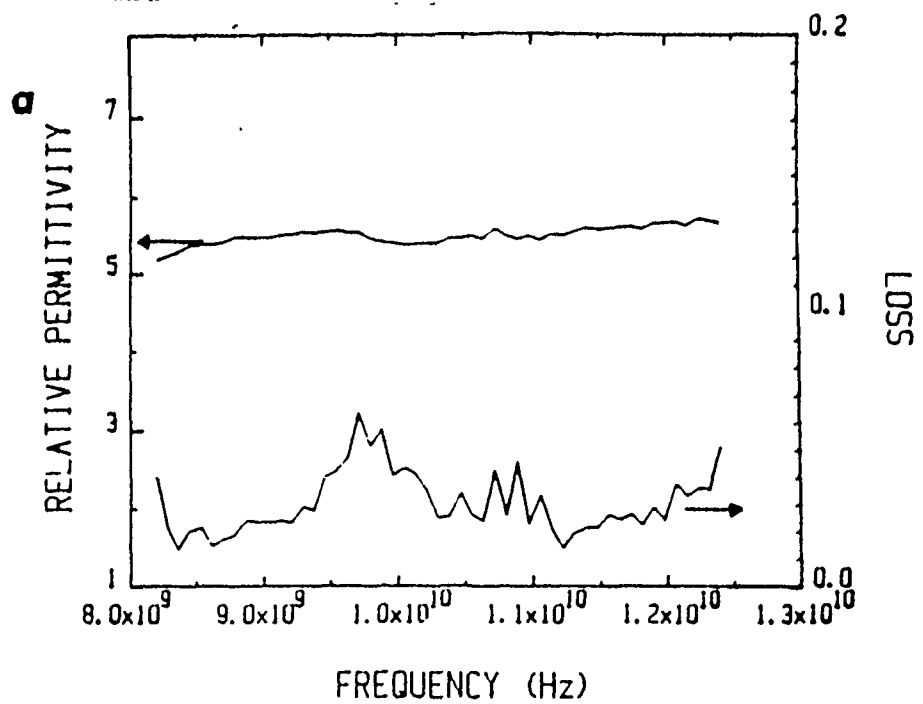


Figure (A)2.2 Schematic for longitudinally loaded dielectric sample in waveguide used to measure the relative permittivity at microwave frequencies.



Figures A(2).3 (a) 3 (b) Electrical response at microwave frequencies of composites with (a) 10 and (b) 20 wt% Cab-O-Sil

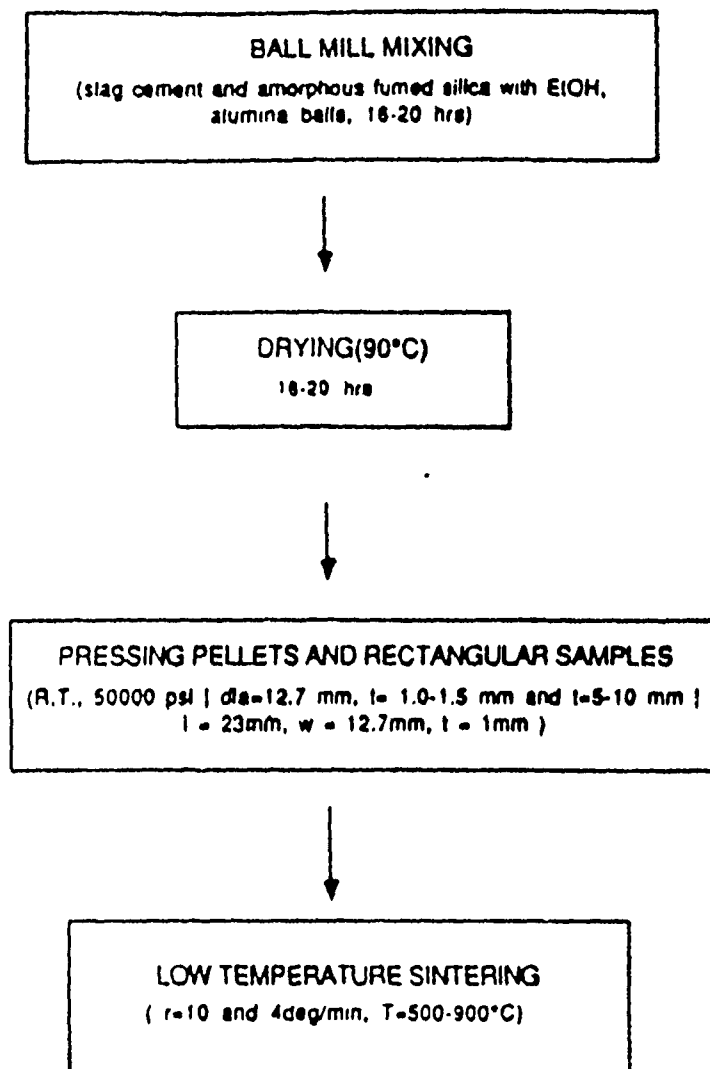


Figure A(2).4 Processing of Slag Cement and Amorphous Fumed Silica.

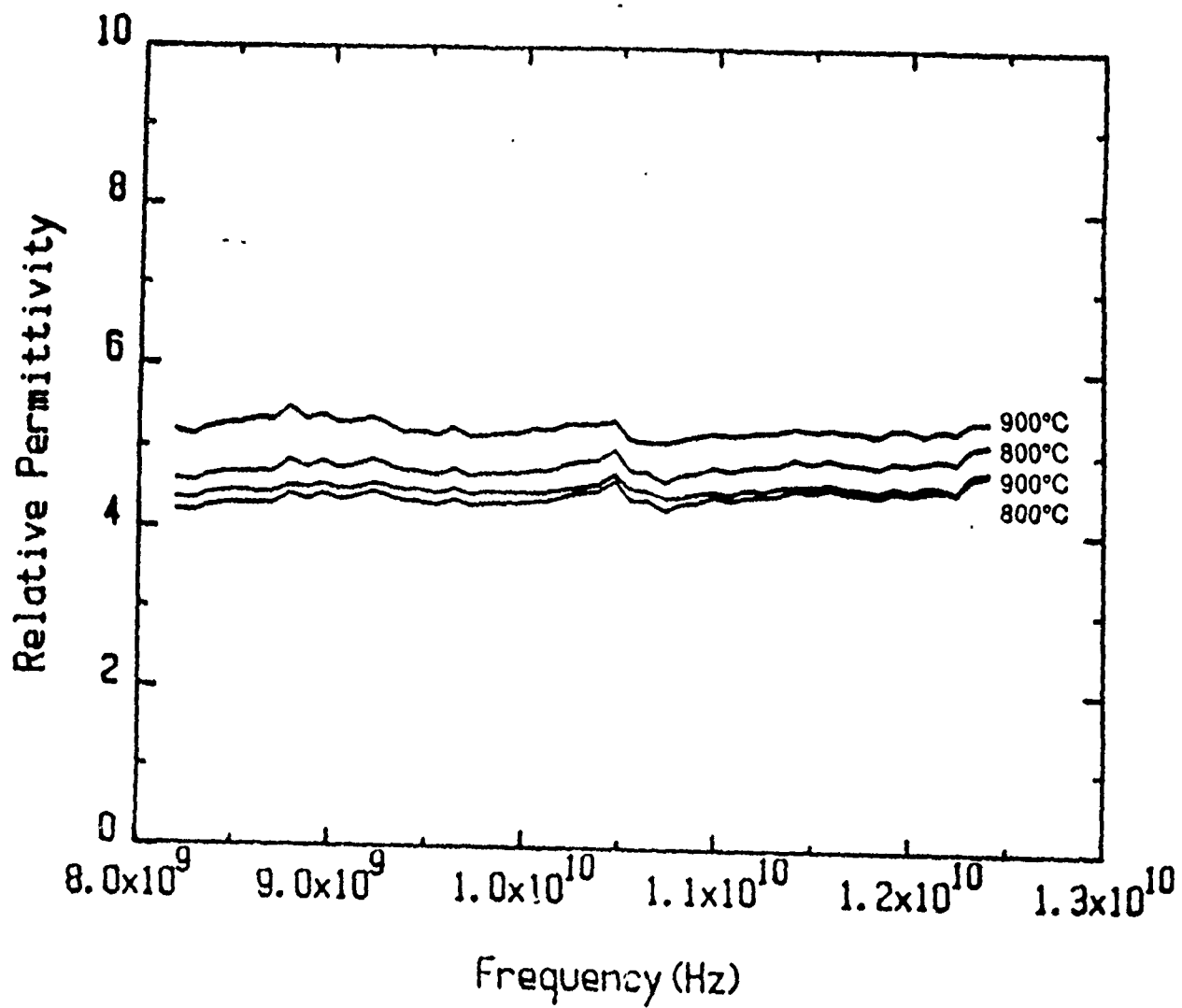


Figure A(2).5 Dielectric Permittivity in the microwave frequency range of MC500 materials with 20 wt% Cab-O-Sil and 10 wt% Cab-O-Sil.

identify elemental constituents, respectively. X-ray diffraction revealed no crystalline phases in either powder. The major constituents of the lead glass frit were 67 wt% PbO, 11.6 wt% SiO₂, and 17.3 wt% B₂O₃. The alkali ion content was ≤ 0.2 wt% for both glasses. Table B1 contains information on the SiO₂ HGM powder. The SEM micrograph of the HGM powder in Figure B.1(a) shows the particles have a spherical morphology and an average particle diameter of ≈ 80 μ m, although the particle size distribution is wide. The lead glass particles shown in Figure B.1(b) are irregularly shaped and ≤ 10 μ m in size which are typical results for a ground frit.

B.2 Specimen Preparation

All specimens were prepared from a batch consisting of 10 vol.% lead glass powder and 90 vol.% SiO₂ HGM; equivalent to 70 wt.% and 30 wt.%, respectively. Powders were dry mixed manually in a glass beaker with a glass rod. 30 wt.% of a PVA binder solution (20 wt.% PVA dissolved in distilled water) was added and stirred until absorbed. The mixture was dried at 100°C for 30 minutes followed by Spex milling for 5 minutes. The milled powder was uniaxially pressed at 35 MPa in a half-inch diameter stainless steel die. After milling, the powders were examined microscopically to determine the extent of SiO₂ HGM breakage.

To burn off the PVA, the pellets were fired at 350°C for one hour, then heated to the desired sintering temperature for a two hour soak. All samples were fired on MgO setters in flowing air. The soak temperatures used were sufficient for the samples to obtain closed porosity yet limit warpage.

B.3 Dielectric Results

The dielectric permittivity of these HGM composites seem to be sensitive to the firing temperature, as shown in Figures B.2 and B.3. Dispersion of permittivity was absent and the losses decreased to less than 0.5% at kHz frequencies. The dependence of permittivity on volume fraction porosity best followed Maxwell's mixing rule. The porosity ranged between 55-68% and was believed to be primarily due to loose packing of the broken HGMs and the irregularly shaped lead glass frit. The lead glass frit had a permittivity of around 14, which caused the permittivity of the composite to be between 3.28 and 3.93, even though the porosity was greater than 50%.

In addition to this work on pressing and sintering disc, some initial work has been done on tape casting HGMs with lead glass frit, using CERBIND (CB73140) cladon binder system. The following flow chart describes the work:

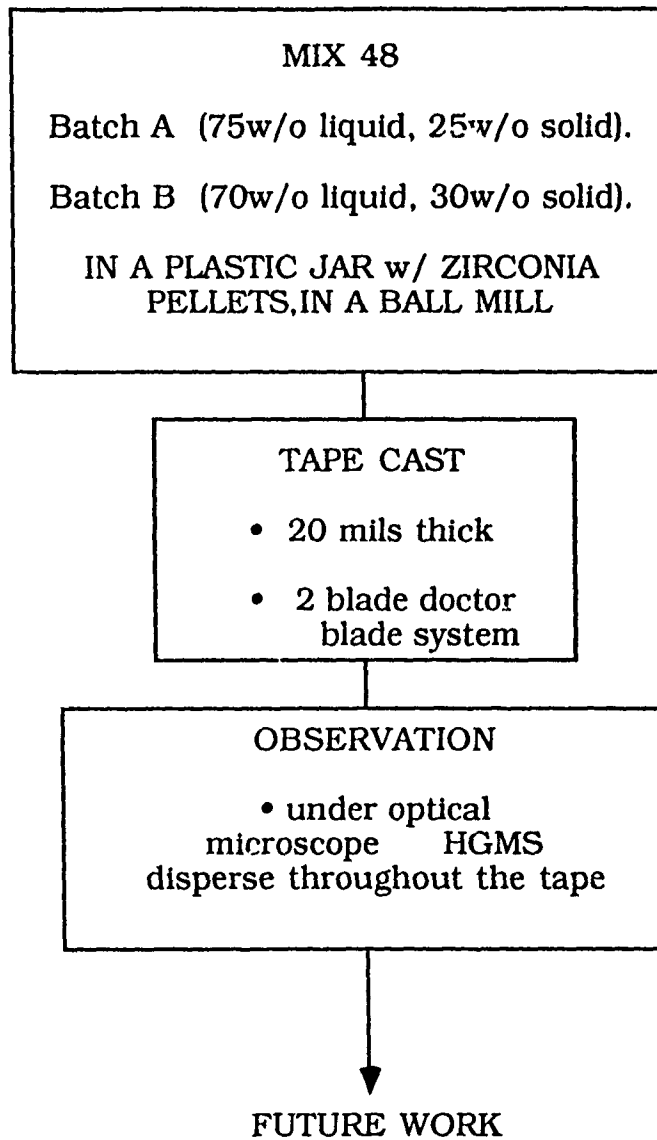


TABLE B1

Information of Eccospheres SI Silica Hollow Glass Microspheres

Chemical composition (wt %):	90.2% SiO ₂ , 0.67% B ₂ O ₃ , 0.19% Fe ₂ O ₃ , 0.19% Na ₂ O, 0.13% CaO, 0.216% (Al ₂ O ₃ , K ₂ O, MgO, TiO ₂), <0.007% (MnO, P ₂ O ₅ , SrO), loss on ignition:5.42%
Average particle diameter (weight basis):	80 µm
Average wall thickness (weight basis):	1.5 µm
True particle density (liquid displacement):	0.254 g/cm ³
Bulk density:	0.152 g/cm ³
Softening temperature:	980°C
Dielectric constant (1MHz to 8.6 GHz):	1.2
Dielectric loss (1MHz to 8.6 GHz):	0.0005

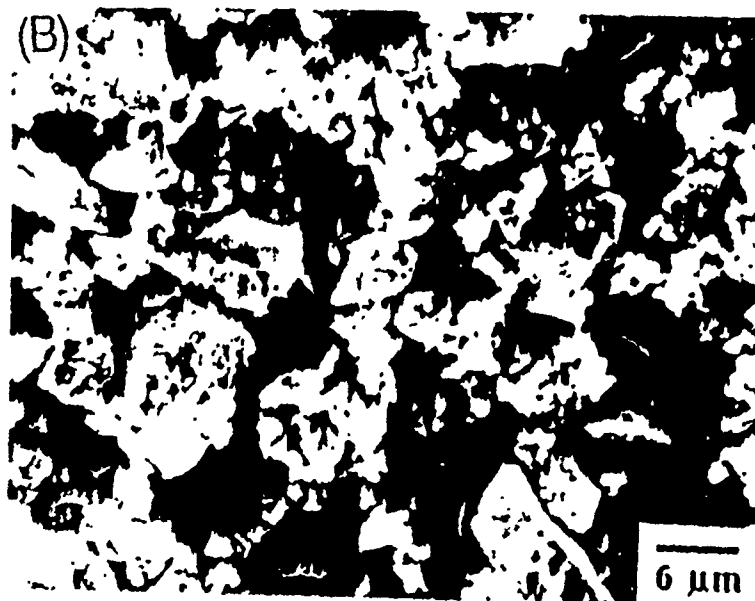
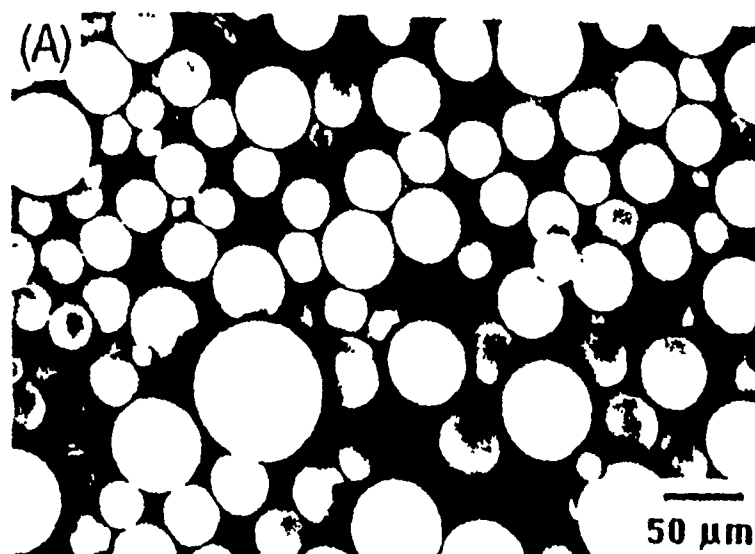


Figure B.1 SEM micrographs of (A)SiO₂ hollow glass microspheres (B) lead glass powder.

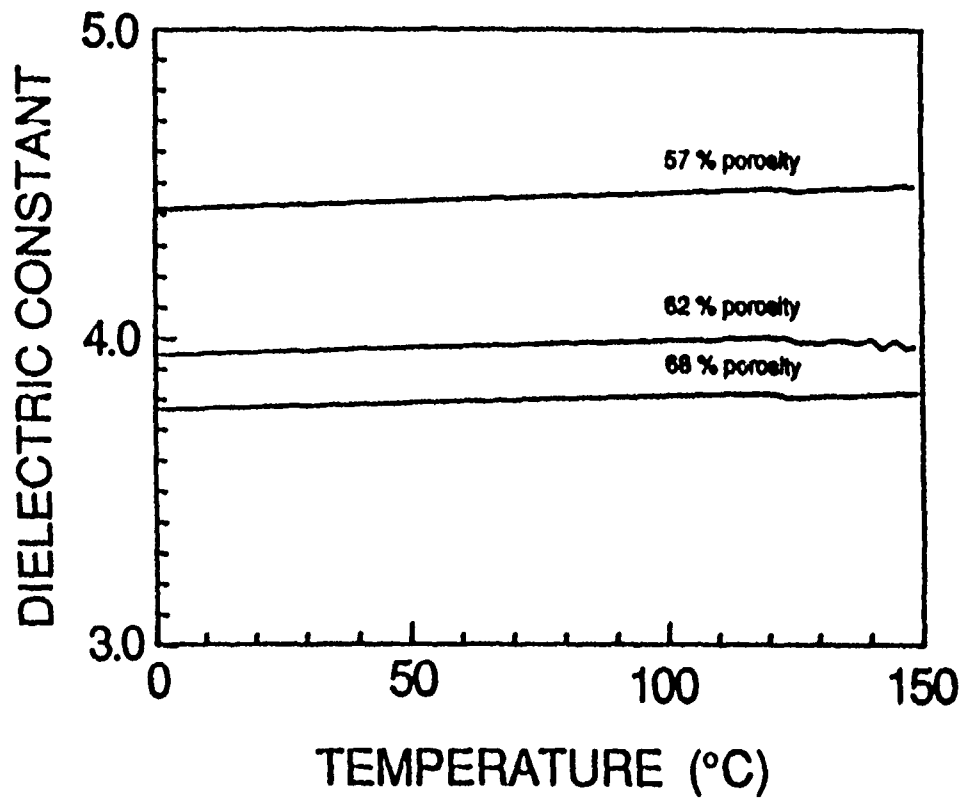


Figure B2 Dielectric constant vs temperature for lead glass/SiO₂ HGM composites fired at 530, 540, and 550°C for 2 hours.

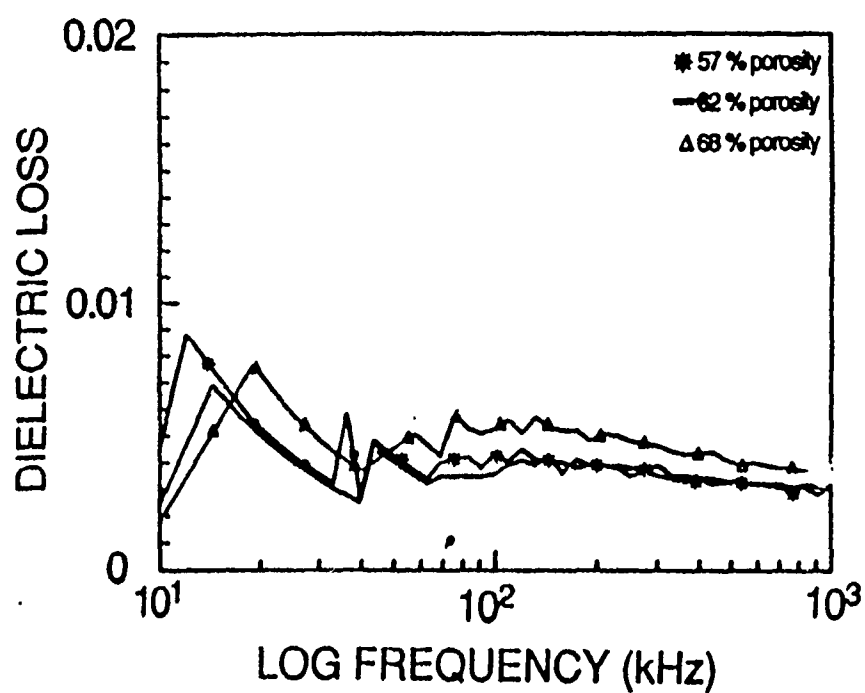
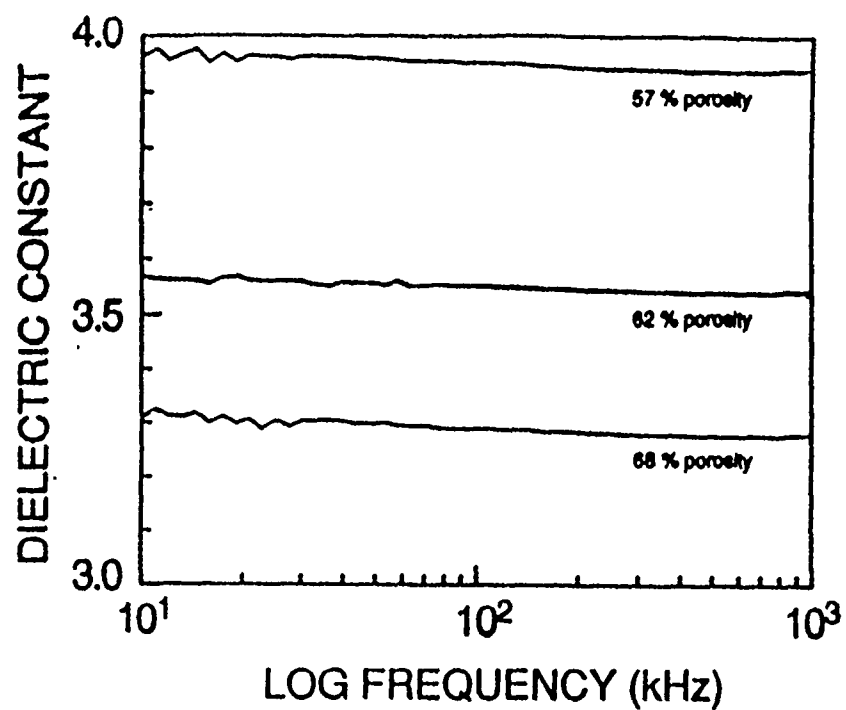


Figure B3 a) Dielectric constant, and b) Dielectric loss vs frequency for lead glass/SiO₂ HGM composites fired at 530, 540, and 550°C for 2 hours.

(C) SOL GEL APPROACH

(1) A study using commercial Ludox (AS-40) sol mixed with PVA was conducted by Umar Mohideen (graduate student) with guidance from Dr. R. Roy.

Experimental Process

A commercial Ludox AS-40 sol (DuPont, Wilmington, DE) was mixed with 3 weight percent polymer solution [PVA, gelatin, cellulose ether or albumin]. The viscosity of the solution was allowed to increase through the evaporation of water. When the viscosity reached 10-100 poise, the solution was applied on a low resistivity (0.001-0.006 ohm-cm) silicon substrate (Pensilco Corp., Bradford, PA) and spun at 2000-3000 rpm for 5 minutes. The film was dried in open air for 12h to allow shrinkage through evaporation of water and then dried at 100°C to get rid of residual water present. The polymer network provides the mechanical strength to the colloidal gel during the drying process thereby overcoming the cracking behaviour. A judicious combination of different molecular weights of the polymer is chosen to adjust thickness and pore volume. The film was heated at the rate of 2°C/min to 600°C and held there for about 1h. Even temperatures as low as 350°C could be used for firing if a continuous flow of oxygen is used in the furnace. The thickness of the films were measured using both profilometer and a scanning electron microscope.

Refer to figure C(1)1 for a flowchart of the process.

Conclusion

The above mentioned process produced porous silica films which had 40% porosity. The thicknesses of the films ranged from 1-10 mm and the dielectric permittivity was found to be around 2.5, with losses less than 1%. Refer to Figure C(1)2. The firing temperature was around 600°C, which allows the use of low resistivity conductors like silver and copper for metallization.

PROCESS

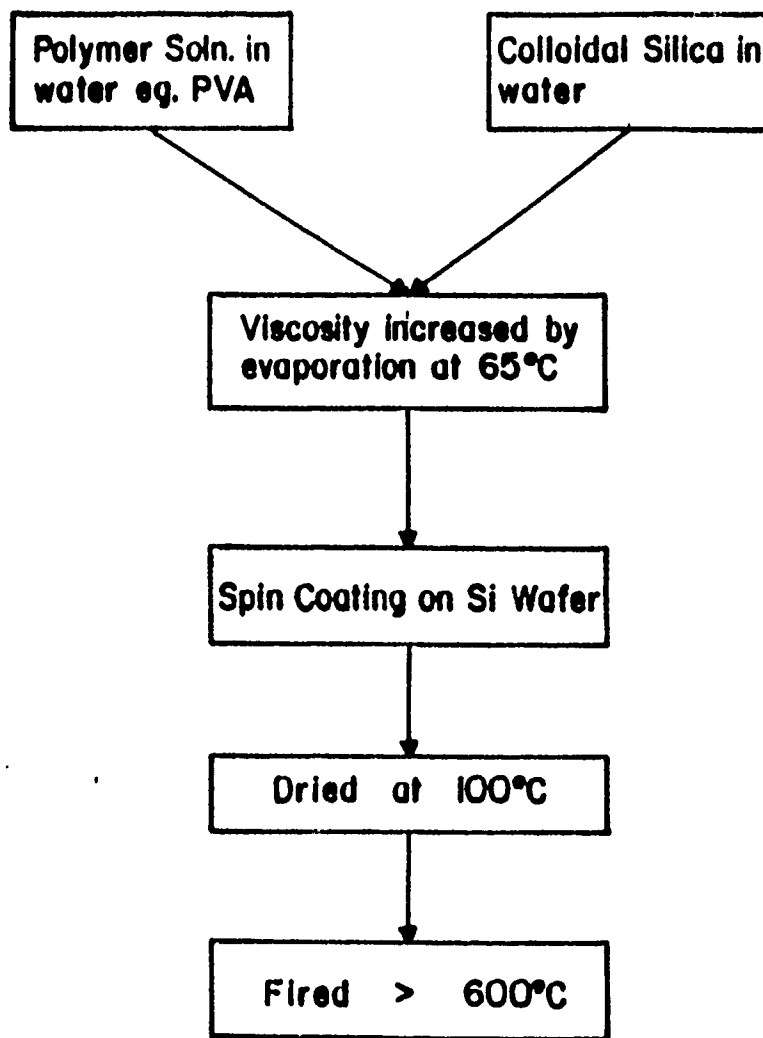


Figure C(1)1

Flowchart showing the sol-gel process using Ludox (AS-40) and PVA.

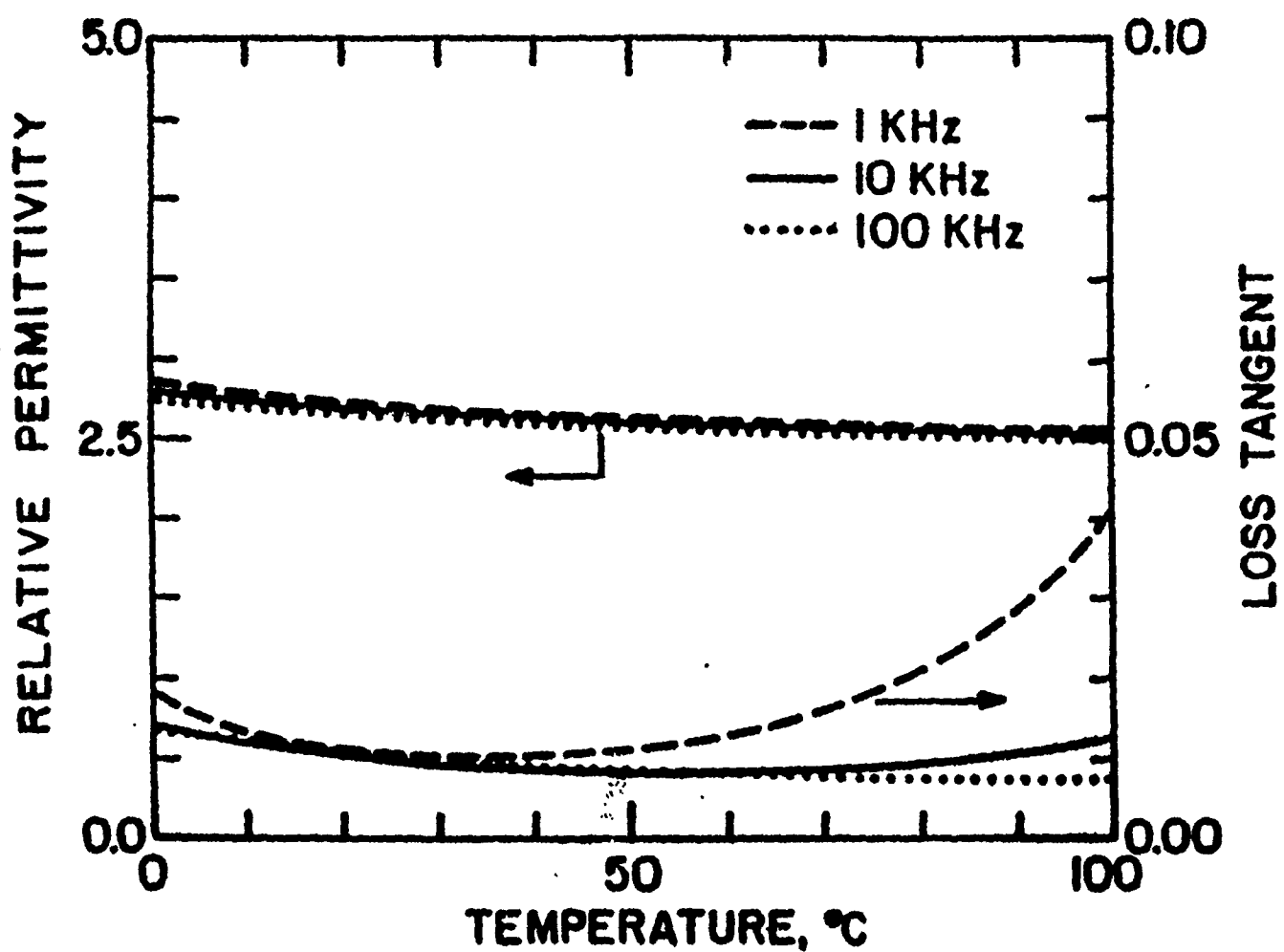


Figure C(1)2 Dielectric onst and loss tangent as a function of temperature for sol-gel derived films.

(2) Another sol gel approach using Cab-O-Sil and latex and ludox (HS-40 and AS-40) and latex mixtures was studied by Jean-Francois Pasquier (visiting research assistant) at Penn State. The two routes, namely the Cab-O-Sil route and Ludox route are described below.

Cab-O-Sil Route

The Cab-O-Sil powder and the water are mixed with a high shear rate mixer (Super Dispax SD-45N). The standard proportion is 25 wt.% SiO₂. The sol is stabilized by a base (Tetramethylammonium hydroxide 25 wt.% in water). A certain percentage of Latex (40 to 60 wt.%) is added to the SiO₂ sol to obtain the coating product.

The first tests of spin-coating on the silicon wafers as substrates have been done directly but, for the chosen compositions, a centrifugation has been found necessary. The coatings without centrifugation have plenty of spots, due to the big agglomerates of silica. With the centrifugation (10 mn, 30 grad. on a Sovall-Superspeed Centrifuge SS-1) the coating are greatly improved.

But the centrifugation requires the use of several coatings in order to reach the thickness of about 10 µm (the viscosity of the supernatant is much lower than the one of the sol without centrifugation : below 20 cP compare with 50 to 100 cP). Thus, a average of 5 layers is necessary to have 10 µm of silica on the silicon wafers.

The multi-coatings have been carried out as follow: the wafers are spin-coated with the supernatant, then dried at 65°C for a couple of hours and spin-coated again. When the number of layers is sufficient (3 to 5), the multi-coated wafers are dried a last time and fired at 900°C for 12 hrs.

The obtained surface is porous and, for a good accuracy in the dielectric measurements, a well-determined flat surface is needed. Thus, a very thin Accuglass coating can be added on top of the silica coating. The Accuglass coating allows to have a good flat surface; moreover it is very thin (0.2 µm) and has a dielectric permittivity of 3.8-4. It has to be heated at 450°C or 850°C according to the kind of Accuglass used (resp. Accuglass 305 or 102). The Accuglass coating could be done before or after the silica coating (in the case where the Accuglass deposit is done before, the firing temperature will be 850°C instead of 900°C and Accuglass 102 could only be used).

For the characterization, gold electrodes are laid by sputtering on both sides of the samples (surfaces of the electrodes : $2.85 \times 10^{-4} \text{m}^2$ or $1.767 \times 10^{-4} \text{m}^2$). A small spot of silver paint is made on each electrode.

Figure C(2)1 is a flow chart describing this route.

The Cab-O-Sil Route.

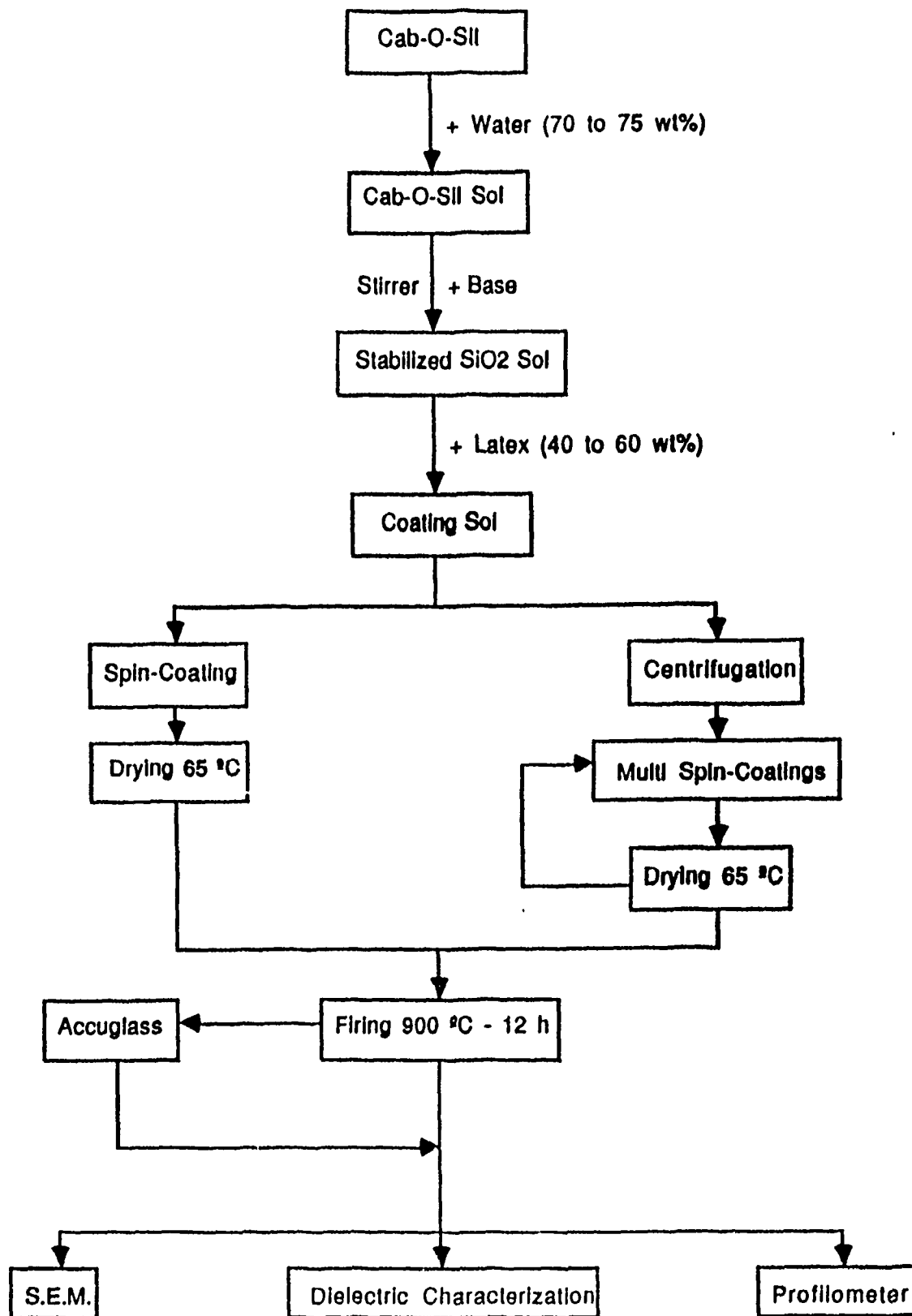


Figure C(2)1 Flowchart for Cab-O-Sil Route.

Ludox Route

"Ludox Colloidal Silica" is an aqueous colloidal dispersion of silica particles. Thus the process is slightly different from the one used for the Cab-O-Sil. Two types of Ludox have been tested : Ludox AS-40 and Ludox HS-40. Some original dispersions have been diluted in order to have the same 25 wt.% of silica than for the Cab-O-Sil sols. But, tests have also been done with 30 and 40 wt.% of silica. These SiO_2 sols are mixed with the latex (Lucite) to obtain the coating sols (40 to 60 wt.% of latex like for the Cab-O-Sil). The viscosity of these coating sols are much lower than the one of the Cab-O-Sil based coating sols (below 20 cP). Thus, it is necessary, in order to have a thickness of 10 μm after centrifugation, to put up to 8 layers on the silicon wafers.

The end of the procedure and the characterizations are exactly the same than the Cab-O-Sil coatings.

Figure C(2)2 is a flow chart describing this route.

Results

The Cab-O-Sil/Latex route produced films of lower dielectric permittivity and loss, as can be seen from Figures C(2)3(a) and (b) and C(2)4(a) and (b). These films had very porous surfaces and penetration of gold through the pores during electroding for dielectric measurement was a problem.

(3) A colloidal sol-gel route was studied by W. Yarbrough (graduate student) under the guidance of Dr. R. Roy. Two different types of substrates were prepared. One was the fabrication of bulk gels (squeeze gels) and the other was the preparation of silica coatings. The sol preparation before gellation was as follows:

Sol Preparation

The source material was a relatively low surface area, high purity pyrogenic silica. Silica sol was prepared using either acid (HNO_3 at pH ≈ 3) or base (tetramethylammonium hydroxide at pH 9 to 11) stabilization. The silica was added to deionized water in portions while mixing in a high shear rate mixer. Acide or base was added in portions as needed to adjust pH and inhibit gelation. Sols were prepared to be 15 to 25 wt.% in SiO_2 . Acide-stablized SiO_2 sols prepared using pyrogenic silica gelled at ≈ 20 to 30 wt.% solids on standing at room temperature for 24 to 72 h. Such gels were reconverted to sols by simple shaking of the container or tapping on a bench top. Base-stabilized silica sols were indefinitely stable.

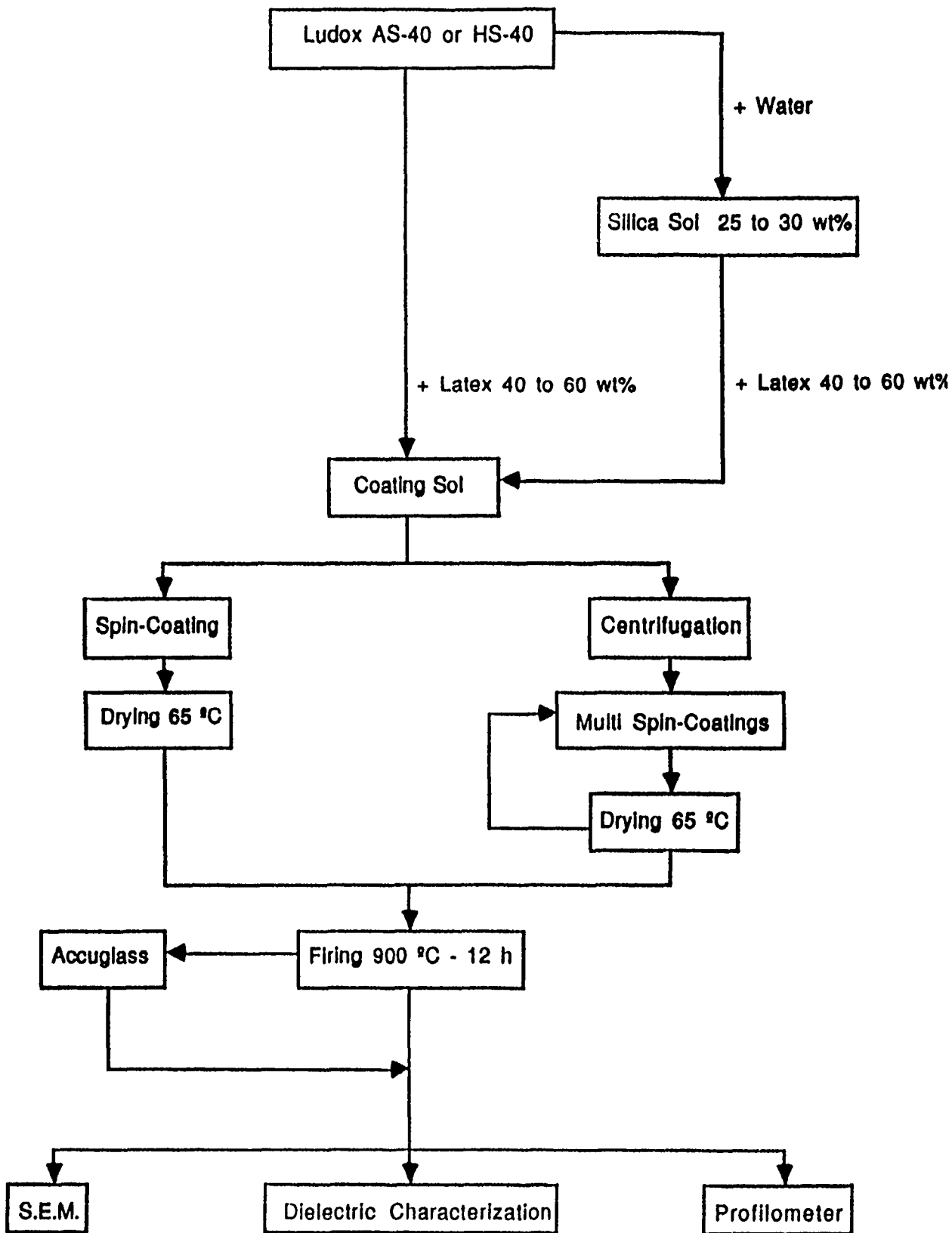


Figure C(2)2 Flowchart for Ludox Route.

Dielectric Characterization of Cab-O-Sil Based Film.

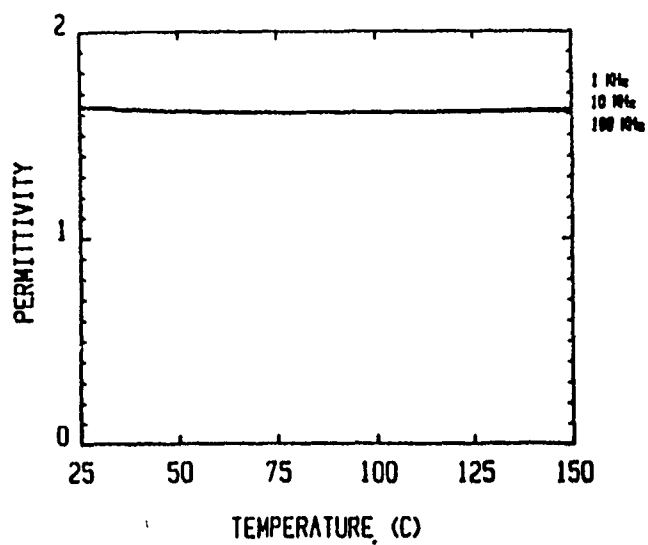


Fig. N° 4-a

Dielectric Permittivity versus Temperature.

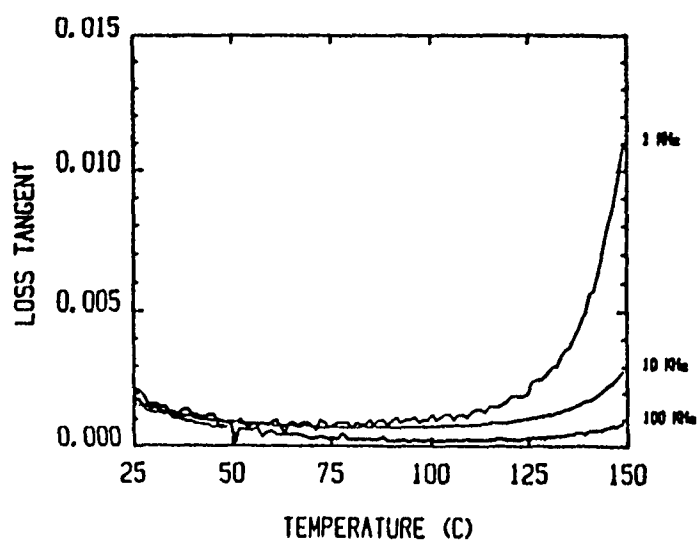


Fig. N° 4-b

Loss Tangent versus Temperature.

* : Film of 14 μm , 5 coatings.

The bulk gel (squeeze gel) preparation is described below. Interamics is currently using this process for manufacturing substrates. (P.T.O.)

Bulk Gel Preparation

These sols were readily converted to gels or gelatinous suspensions by simple adjustment of the pH to neutral using either ammonia or HNO_3 . We found it readily possible to fabricate samples for measurement by pressing in porous graphite molds. Three different presses were used. The first of these consisted simply of graphite plugs, machined on a lathe to fit tightly (<50 kg press fit) inside a steel pellet press 2.54 cm in inside diameter. These plugs were ≈ 2.54 cm long. The ram and bottom plug were made of steel and each had a sliding fit to the bore of the press body, leaving sufficient clearance for fluid to pass between them and the press body. The graphite plugs were used between the steel ram and base plug. Samples of gel were pressed between the graphite plugs, using a common lab hydraulic press, at nominal pressures of 44 to 88 MPa. The load was applied in stages over 3 to 5 minutes, allowing time for fluid to flow, as evidenced by a reduction in the hydrostatic load read from a gage on the press. Fluid passed easily into the graphite and between steel surfaces to the outside while the silica gel was retained between the graphite plugs. A second press used was constructed entirely of graphite and consisted of a base 3 cm in diameter by 1 cm thick, on top of which was placed a press body 5 cm in diameter by 5 cm long, having a 1.6 cm (5/8 inch) bore. The piston for this press was 5 cm long and was turned on a lathe to fit tightly in the bore for ≈ 1 cm of its length at one end, the remainder of the length being a sliding fit to ensure easy extraction. Gel samples were pressed at loads not exceeding 88 MPa. The third of these consisted entirely of graphite and was a 3-cm outside diameter cylinder, ≈ 5 cm long, with a 3-mm inside diameter hole drilled through the center. Plugs, 5 to 8 mm long, were turned on a lathe to fit the bore. A piece of steel drill rod, slightly smaller in diameter than the bore, served as a piston. This press was used to prepare rod-shaped samples measuring 3 mm in diameter by 7 to 12 mm long for dielectric measurements at microwave frequencies.

Much of the interstitial water is removed in the pressing operation, and evaporation of the remaining pore fluid did not result in measurable dimensional change. Silica gels prepared in this manner can be calcined at 900°C without dimensional changes $>1\%$. The silica gels will sinter to transparent to translucent noncrystalline bodies upon calcination at temperatures exceeding $\approx 1100^\circ\text{C}$ for periods exceeding 2 hours. For this work, only minimal sintering to achieve sufficient mechanical integrity for handling, electroding, and property measurement was desired. This requirement was achieved using temperatures 900° to 1000°C for 5- to 12-h periods. Low temperature processing not only retained much of the original gel porosity, but also would

conceptually permit the use of Cu, Ag, or Au metallization for high speed signal layer traces in an ultimate package configuration. Densities were calculated from measured weights, thicknesses, and diameters. Volume fraction porosity was estimated from the measured density, taking 2.20 g/cm^3 to be the density of vitreous silica.

Preparation of Silica Coatings

A successful technology for very high density, high speed packages must provide for the fabrication of signal-layer dielectrics as thin as $\approx 10 \text{ }\mu\text{m}$ with provision for vias between signal layers of ≈ 25 to $100 \text{ }\mu\text{m}$ in diameter. Good planarization of the supporting structure is a necessity. These fine geometries rule out many of the conventional ceramic processes, e.g. mechanical punching of vias and screen print metallization.

The objective was to find a formulation or formulations which would allow the preparation of thin gel coatings (≈ 5 to $50 \text{ }\mu\text{m}$). The central difficulty is, of course, the tendency of colloidal sols toward premature gelation and skin formation on drying. Such gels are normally of low density, weak and brittle. The interfacial tension of the pore fluid with the atmosphere is normally much larger than with the solid, and the pore radius is normally quite small ($\ll 1 \text{ }\mu\text{m}$). These effects give rise to surface tensions that can be much larger than the tensile strength of the gel. This behaviour leads to the familiar cracking and peeling of the gel layer as it resists further shrinkage on continued evaporation of the pore fluid. Many polymers also exhibit skin formation on drying from solution, but typically these are viscoelastic and will easily relax to dissipate local stresses. However, as skin formation occurs, the rate of solvent removal is dramatically reduced and drying or setting times can become excessive. Heating to enhance drying can often result in blister or bubble formation which in this application is clearly intolerable even on a very fine scale.

In this work, it was found possible to avoid some of these difficulties by using an acrylic latex used commercially as a paint base. The latex is a copolymer formulation of methylmethacrylate and 2-ethylhexylacrylate containing 2 mol% methacrylic acid. Hence the latex is stabilized with ammonia at a pH of ≈ 9 and is stable to higher concentrations of base, where a silica sol prepared with tetramethylammonium hydroxide or other suitable base is also stable. A coating formulation was found using the proportions given above and it was found that this could be cast and dried either as coatings on suitable substrates (e.g., silicon wafers) or as castings on a nonadherent surface (teflon) which would allow for tape or film formation. For thick layers it was found necessary to add humectants or plasticizers, polyethylene glycol proving satisfactory in the present case. Coatings were prepared by spin or dip coating Si wafers with a formulation consisting of 70% polymer and 30% silica, on a solids weight basis. These coatings were readily dried at temperatures ranging from ambient to 65°C . Polyethylene glycol was used as a humectant

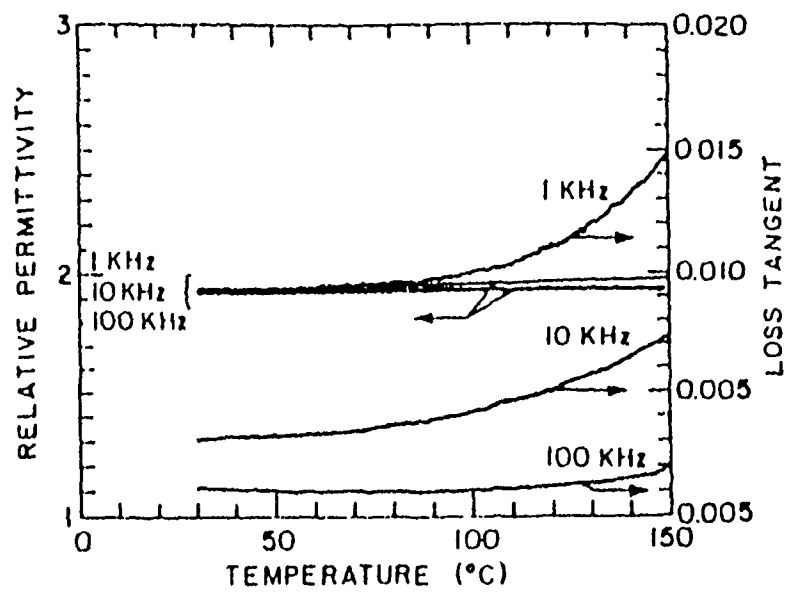


Figure C6 Relative permittivity and dielectric loss versus temperature for 17-mm-thick SiO_2 film.

and plasticizer for the thicker coatings. These coatings showed good adhesion to silicon and were fired at 900°C for 12 hours without cracking. Fired film thickness in the range of ≈ 5 to 50 μm were prepared.

(D) REACTIVE SPUTTER DEPOSITED SUBSTRATES

A morphological study of reactive sputter deposited SiO_2 films was conducted with two goals in mind. The first was to study the effect of thickness on dielectric properties. As can be seen from Figure D1, the permittivity increases from 2.6 to that of bulk silica with increase in thickness of the films. The postulate that tries to explain this, is the nucleation of dense clusters during the growth process. The second aim was to study the surface roughness of the silica films on different substrates to determine whether they could be planarized for putting down fine signal traces using photolithography. For planarization, which is done using a spin-on glass (Accuglass 305, from Allied Corp.) is very critically dependent on the surface roughness of the films. In order to achieve planarization, the roughness should be of the order of the thickness of the planarizing film. Since the max^m crack free thickness of these coatings is about 3000Å, the roughness* should be of that order.

(E) METALLIZATION

Metallization on sol-gel and reactive sputter deposited substrates have been attempted using photolithography. Metallization using screen printing is being investigated on the tape cast substrates and other bulk (squeeze gel) substrates at Interamics.

Photolithography: Test coupons developed at Mayo Foundation have been used to lay down Aluminum signal traces, with microstrip geometry. The metal traces varied in width from 0.25 mils to 1.5 mils (6 to 37.5 μm) and the separation ranged from 0.25 to 0.1 mils (6-25 μm) and the separation ranged from 0.25 to 0.1 mils (6-25 μm). The signal traces on unpolished alumina substrates were found to be discontinuous under the optical microscope. However good continuous signal traces were laid down on single crystal silicon substrates and planarized elkanite substrate. Refer to Figures E1 and E2.

GEOMETRY OF SIGNAL TRACES

The signal traces had a rectangular cross section with width varying from 6 to 37.5 μm and the thickness of the aluminum film (evaporated) was about 2000Å (0.2 μm). The length of these traces was about 4 cm. This made the resistance measured across each tract very high (about 560Ω). This would be unacceptable for measurement of crosstalk at the Mayo Clinic, with a load of impedance of 50 Ω. For matching a load impedance of 50 Ω, the line impedance should be less

than 5 Ω (personal comm. of Barry Gilbert). Therefore the focus switched to putting down thicker metal films traces on the substrates. From Figure E3, for 5 Ω aluminum line resistance, it was determined that at least 5-10 μm thick metal traces was necessary. This became a limiting factor for metallizations.

Attempt 1: At Penn State, we were able to vacuum evaporate 5-10 μm thick aluminum film on the low K silica films, but chemical etching of these thick aluminum film, during photolithography was impossible. The resist pattern was removed before the etchant could penetrate 5-10 μm .

Attempt 2: Another attempt was made by trying to reactive ion etch (RIE) the aluminum film. The selectivity of RIE was used this time at Enerjet, Kurt J. Desker Company. The etching gas and conditions are shown in Table E1. The results again were the same as before and the suspicion was that thick Al films contained a lot of oxide which was difficult to etch; this was surmised from the milky white color of the thick aluminum films.

Attempt 3: This time a completely new approach was envisioned. We tried to electroplate gold on top of thin aluminum traces. This was unsuccessful because of the poor adhesion between the aluminum and gold. Therefore electroplating was attempted on a gold film on the silica substrate. The film did not withstand the attempt. Finally a thin film of Nickel (1500 \AA) was used before putting down a gold film (2500 \AA) on top of it. Then the electroplating was done on the gold for 45 minutes and a thick film 5.3 μm of gold was achieved.

(F) VIA FORMATION

The first attempt at forming vias in these low k substrates was by W. Yarbrough.

Photolithographic processing is alternative option for the formation of vias and other structures. In the case of the gel derived materials of the present work we found it possible to impregnate the coating with photoresist, expose, develop etch the coating where the resist was removed in development, and remove the remaining resist of obtain a finished patterned piece.

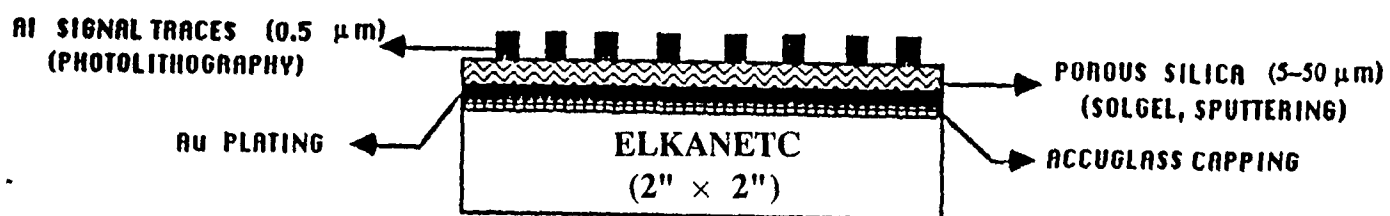


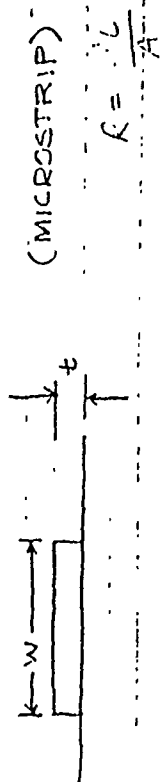
Figure E1



Figure E2

GEOMETRY OF SIGNAL TRACES FOR 5Ω LINE RESISTANCE, USING AL

SIGNAL TRACES



[FOR 5Ω RESISTANCE (R)]

[FOR ALUMINUM, (ρ) RESISTIVITY = $2.824 \times 10^{-6} \Omega \cdot \text{cm}$]

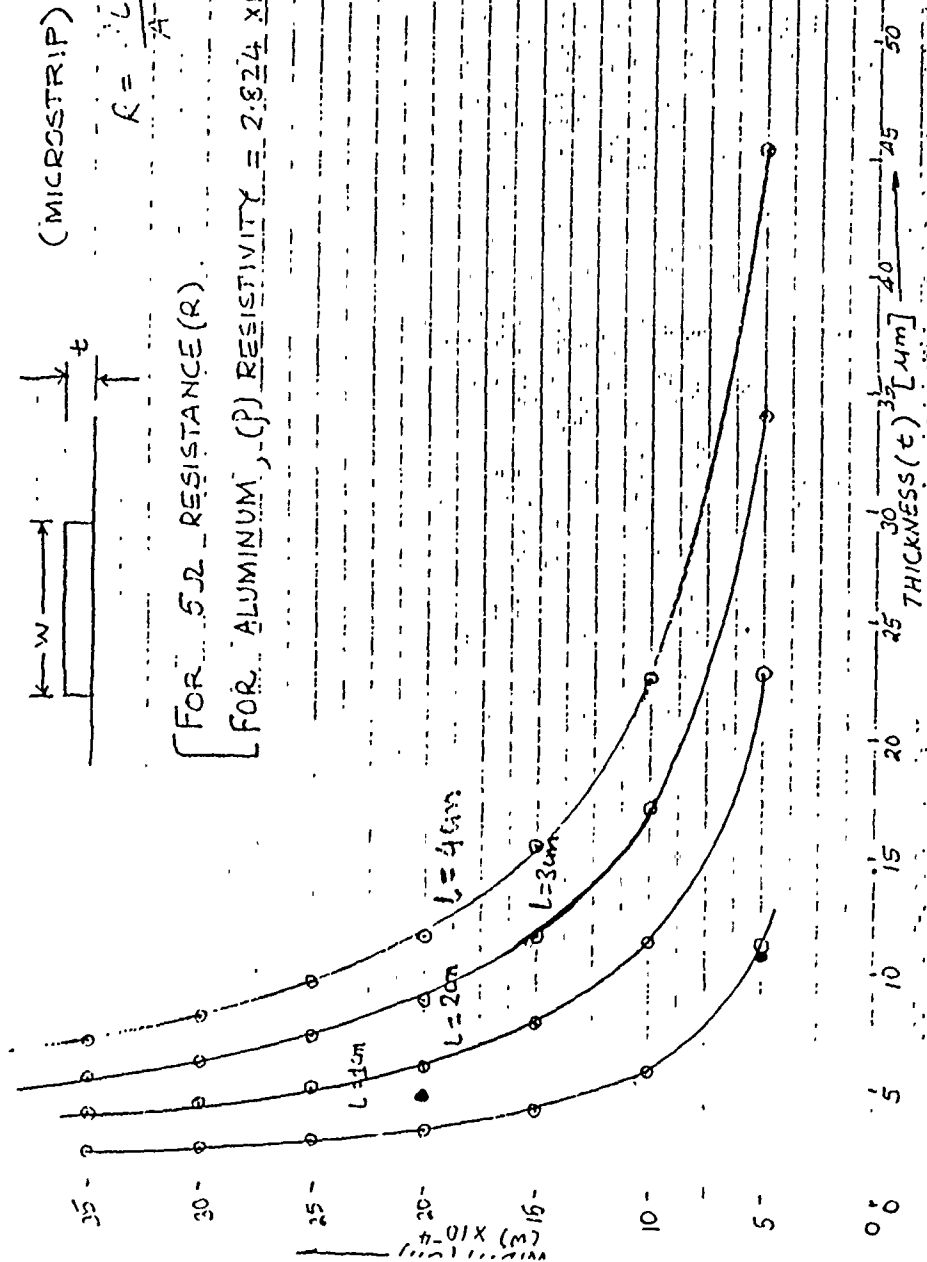


Figure E3

TABLE E1

Etchine Conditions

Flow BC13	=	16.55 ccm
FlowC12	=	4.4 ccm
Total Pressure	=	14 mTorr
RF Power	=	100 watts
Time	=	13 minutes
Type Etch Rate	=	2000Å/min

The photoresist and developer used are commercially available* and are widely used in the preparation of integrated circuits. Etching of the silica was readily achieved using a 20% hydrofluoric acid solution. The remaining photoresist was then stripped with HPLC grade acetone.** Figure 9 shows the pattern after exposure and development, but before etching of the silica and stripping of the photoresist. Exposure was accomplished in 15 minutes using water filtered radiation from a 400 watt Hg arc lamp source. The photomask was prepared by photographing the pattern with a 35mm camera loaded with black and white negative film. The secondary electron images in Figures 10 and 11 show a finished via and detail at the edge of the via respectively. The coating appears quite uniform in pore structure throughout the thickness exposed by etching. With the relatively crude bench scale processing used in this example, 100 μm vias can be produced. It is reasonable to expect that with better masks, collimated illumination, and better control of particulate contamination, 50 μm and finer size vias will be achieved.

Another technique for the formation of coaxial vias using conventional laser drilling has been attempted by A. Das. The process is pictorially represented in Figure F4. The gold and the silver epoxy were completely isolated by the silica film and the sol-gel cap. Resistivity measurements on 16 such vias proved this. Figures F5 and F6 are SEM micrographs of a fractured edge of the coaxial via, at two different magnifications. It is difficult to find out from these micrographs, whether the cured silver epoxy has defects, isolated pores in it. Further investigation on these coaxial vias is being conducted.

Another interesting finding during the development of vias is that a silica film on the Alumina substrate does form a less cruddy via entrance. This is probably because of the lower melting point of silica, which melts and coats the alumina surface at the mouth of the via. SEM micrographs, Figure F7 and F8 are comparison of vias formed without and with a silica film respectively.

FOOTNOTE:

*Microposit S1400 and developer CD-30, Shipley Co., Whitehall, PA

** Fisher Scientific Co., Pittsburgh, PA

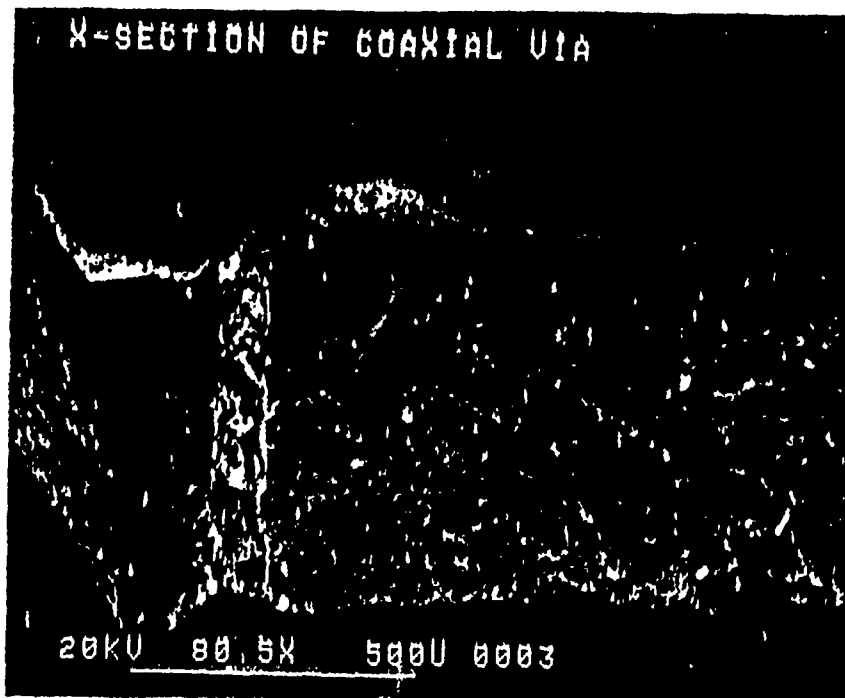


Figure F5 Fractured edge of a coaxial via at low magnification (80.5x).

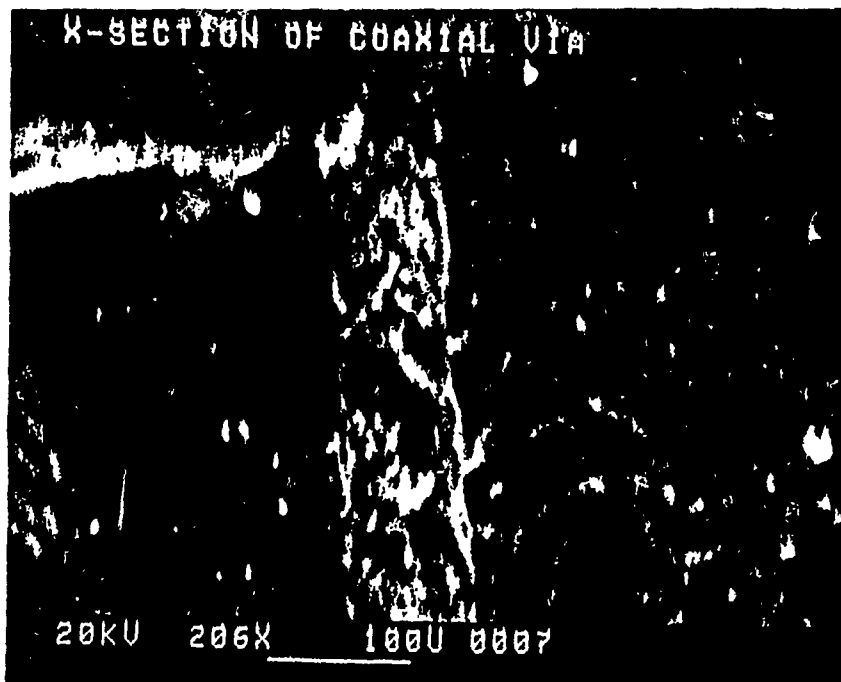


Figure F6 Fractured edge of coaxial via at higher magnification (206x).

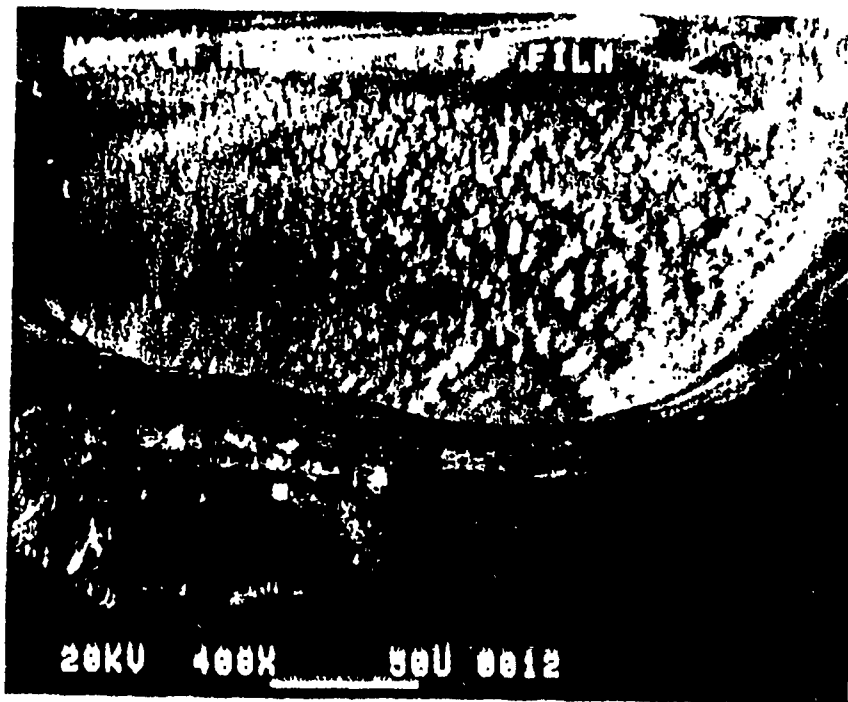


Figure F7 Via with cruddy entrance.

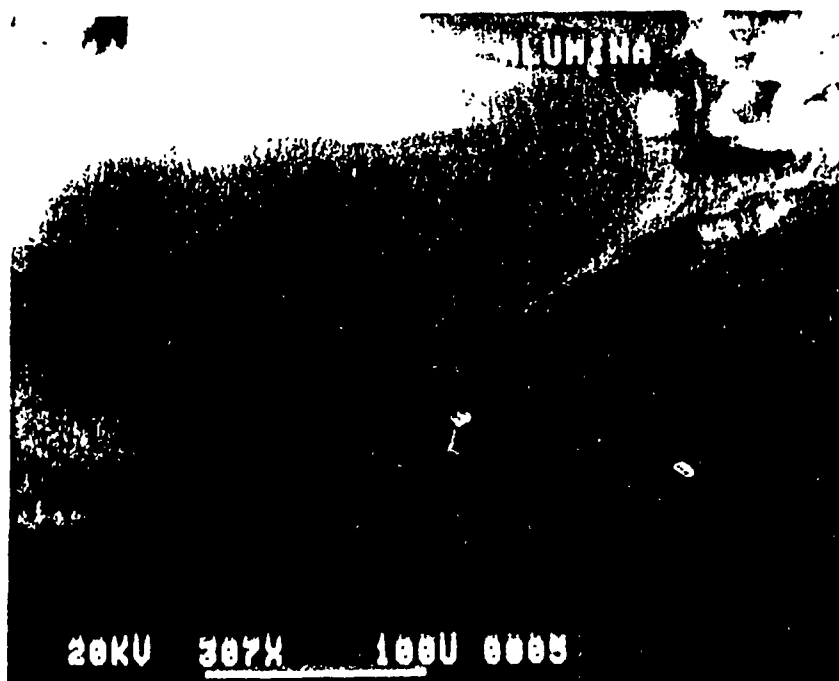


Figure F8 The entrance is smoothened probably by the melting of silica film deering easier drilling.

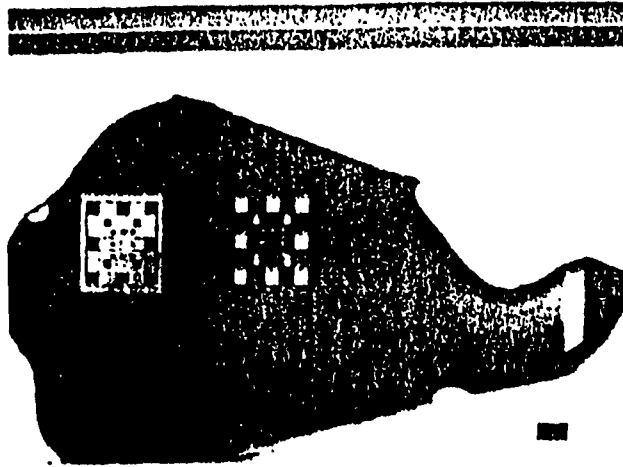


Figure F9 Exposed and developed photoresist impregnated SiO₂ film showing pattern used to test via formation. (bar = 1 μ m).

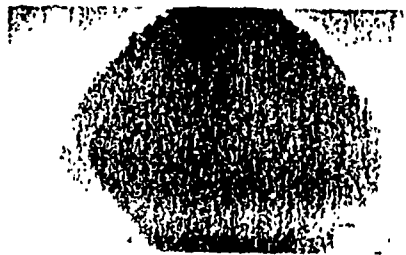


Figure F10 SEM photomicrograph at a ≈ 100 mm via formed in an SiO₂ coating by use of photoresist impregnation and etching of the exposed area. (bar = 20 μ m)

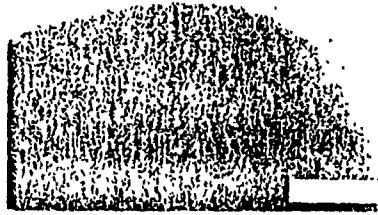


Figure F11 Detail of the etch of the via seen in Fig. F10. Note that the pore structure seen at the surface is uniform throughout the thickness of the coating. (bar- 20 μm).

Formation of a Coaxial via System

Step 1

Laser drill 5 mil ϕ vias in alumina substrate.

Step 2

Sputter deposit. All on the drilled substrates ($\leq 1000\text{\AA}$).

Step 3

Sputter deposit 5 mm thick SiO_2 film.

Step 4

Accuglass cap the sputtered SiO_2 film and then screen print silver epoxy through via while the substrate sits on a vacuum chuck.

APPENDIX 1

2, 3

The Pennsylvania State University

The Graduate School

POTENTIAL AND LIMITATIONS IN THE APPLICATION OF SOLUTION-SOL-GEL METHOD
TO CERAMIC PROCESSING

A Thesis in

Solid State Science

by

Walter A. Yarbrough

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 1988

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ABSTRACT

The potential of the solution-sol-gel method for the preparation of new materials is examined with concentration on ceramic compositions. Because of the inherently irreversible nature of the process, the properties of the products produced are highly dependent on the precise path followed in their preparation. The argument is presented that the greatest potential of the method lies not with the preparation of materials currently available by other means, but rather in the preparation of new materials, with properties which can be tailored to fit specific needs and interests. A wide variety of materials are possible even within the same composition. This is demonstrated by the preparation of several different materials and the means by which the final product may be varied are shown. Alpha aluminum oxide was prepared from alumina gels and the control of microstructure and density by the technique of seeding demonstrated. The refinement of microstructure and concomitant enhanced densification are shown to depend upon the epitaxial or heteroepitaxial nucleation of the stable phase. The one known failure of an isotypic phase, alpha chromia, to seed the formation of alpha alumina at low concentration is shown to result from reaction with the metastable alumina xerogel with the loss of the precursor structure type, prior to onset of transformation to alpha alumina. The preparation of nanocomposites is demonstrated with the preparation of spinel/alumina composites and nanoporous silica. Spinel/alumina composites using both magnesium aluminate and lithium aluminate spinels were prepared showing analogous and unusual microstructural development with the absence of well-defined grain boundaries. The utility of nanoporous gel derived silica for the solution of a current materials problem is demonstrated with the preparation of a low density material having a relative dielectric permittivity of less than two. The dielectric properties of the porous silica nanocomposites are shown to be consistent with Lichtenecker's mixing rule for composites with mixed connectivity patterns. The path of relaxation to lower free energies is shown to depend upon the method and kinetics of gelation with the preparation of gels of the composition of cordierite. These materials show the presence of a liquidus at temperatures well

below the equilibrium melting point of the crystalline composition. In spite of the presence of a low temperature liquidus, the kinetics of crystallization and the products formed are found to be sensitive functions of the method of gel formation. The use of seeding for control of phase formation in this system is demonstrated.

APPENDIX 2

The Pennsylvania State University

The Graduate School

SPUTTER DEPOSITED SILICA FILMS AS SUBSTRATES FOR
MICROELECTRONIC PACKAGING APPLICATIONS

A Thesis in
Solid State Science

by

Amitabh Das

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 1988

ABSTRACT

Microelectronic packaging for high speed (GaAs) and very large scale integrated circuits is facing many problems, most of them being materials related. One of the most important problems is to develop low relative dielectric permittivity and low loss substrates for enhancing signal propagation. In this study sputter deposited silica films were investigated as a possible substrate for signal lines. Silica was selected because it has the lowest relative dielectric permittivity (3.8) and loss ($\tan \delta = 0.0001$) among the inorganic materials.

Various processes were investigated to obtain porous silica films in order to further decrease the relative dielectric permittivity. Reactive rf sputtering was identified as one of the more practical processes. The deposition parameters for obtaining porous films were identified from the structure zone models (SZMs), which are useful guides to preparation - morphology relations. This was a novel approach because porosity was never required for other electronic applications of rf-sputtered silica films.

The dielectric properties of the reactively sputtered films were studied as a function of gas pressure and thickness. To further characterize these films, the internal stresses, stoichiometry (using IR spectroscopy), microhardness, dielectric breakdown and morphology as a function of thickness were studied. From the dielectric data, the porosity in the films deposited under low adatom mobility conditions (bombardment induced) appears to decrease with thickness. The stoichiometry did not change with thickness for the low and high pressure deposited samples. However, the

internal stresses decreased with thickness only for the films deposited under low adatom mobility conditions. The dielectric breakdown decreased with thickness and the microhardness decreased with gas pressure. These were explained by the fundamental inverse relation between porosity and mobility of adatoms.

The final part of this study was targeted towards the fabrication of a prototype package using reactively sputtered silica films. The surface roughness of these films on substrates of different roughnesses were observed with an image analysis system, as a function of thickness. The films tend to mimic the roughness of the substrate; therefore, to planarize the substrate in order to deposit a continuous signal traces, a sol gel capping process was successfully used. To decrease the series resistance of fine line width metal traces on these silica substrates, photolithography and electroplating techniques were used. A novel technique was developed for fabricating coaxial vias to prevent crosstalk between signal lines. Finally wirebondability (thermosonic) on metallizations on these silica substrates was found to be excellent.

APPENDIX 3

The Pennsylvania State University

The Graduate School

THE DEVELOPMENT AND PROCESSING OF CALCIUM ALUMINATE CEMENT
AS A LOW RELATIVE DIELECTRIC PERMITTIVITY MATERIAL

A Thesis in
Solid State Science

by
Paul Sliva

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

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ABSTRACT

This thesis is a survey of calcium aluminate cements and their potential use as a low dielectric constant, low loss electronic packaging substrate material. The first half of the study expounds on the properties of calcium aluminate cements, prepared with poly(vinyl alcohol), as cured cement pastes. The second half of the study enucleates the potential of tape casting calcium aluminate cement and forming sintered laminates.

As a room temperature curable material, the effects of curing conditions, atmosphere and temperature on the density and dielectric properties of cured pastes were confirmed. The dielectric constant of the various cements measured at frequencies less than 1 MHz ranged from 4 to 8. At microwave frequencies, the dielectric constant of SECAR 51, 60, 71 and 80 cured pastes varied from 5 to 7. The real and imaginary parts of the dielectric constant for SECAR 51 and 80, as measured in the far IR, showed many resonance peaks to 40 THz, above which the resonances become clamped. Dielectric losses for all the cements remained relatively stable (~ 0.005) across the frequency range. SECAR 71 and 80 cement cured at room temperature and at 80°C resulted in dielectric constants and losses (at low frequencies) being 40-50% higher for the 80°C-cured cements. The cements cured at 80°C also had densities 70% higher than those cured at room temperature. Dielectric properties of 7-day-old SECAR 71 cement pastes containing 1.8 wt.% poly(vinyl alcohol) and a water-cement ratio of 0.20 were remeasured after their exposure to laboratory ambient atmosphere for 36 months. Dielectric constant and loss at low frequencies (≤ 1 MHz) showed virtually no change between the two cements (K-4-5, $D \sim 0.005$).

Processing to incorporate hollow glass microspheres into the cement was defined. Additions of up to 40 vol.% microspheres into SECAR 71 cement paste resulted in a lowering of the dielectric constant from $\sim 4-5$ to 2.7 (measured at ≤ 1 MHz). Dielectric loss was not affected by the microspheres. The dielectric constant of the SECAR 71

cement pastes containing varying quantities of microspheres can be modelled as a combination of Maxwell's (discrete porosity) and Lichtenecker's (three-dimensional interconnected porosity) dielectric mixing rules.

Several characteristics of cured cement pastes were measured. The flexural strength of air-cured bars was ~ 7 MPa. Microstructural observation showed porous regions throughout the cement, an indication of inadequate particle bonding by the poly(vinyl alcohol). Calculations from the fracture toughness indicated that a flexural strength of 25 MPa could be achieved at a flaw size of 0.1 mm. Thermal conductivity for all the calcium aluminate cements was ~ 1 -2 W/m-K. The thermal conductivity is controlled by the bulk and the porosity in the cured pastes. The role of the poly(vinyl alcohol) was verified per a previous investigator's hypothesis. Using infrared spectroscopy and energy dispersive x-ray analysis, it was verified that the aluminum from the cement is involved in cross-linking the poly(vinyl alcohol).

Properties of sintered SECAR 71 cement were established. Processing parameters were established for vibratory milling of the cement for 48 hours in 95% ethanol. Particle surface areas, slurry viscosity, particle size distribution and relative pH were compared and contrasted over the 48 hours of milling. Slips were prepared with an acetate binder system and milled cement and tape cast at solids loadings of 3.6 vol.% to 31.0 vol.%. Variations in green tape densities were correlated with particle interactions. A volume percent loading of ~ 19 -20 vol.% cement resulted in the highest green density. A binder burnout schedule (up to 600°C over 50 hours), as well as a sintering schedule (1450°C for 1 hour in air), were established to remove residual water and the binder and then to sinter the tape (which was previously laminated). Grain growth and microstructural development were correlated with transverse shrinkage and sintered density ($\sim 96\%$ of theoretical).

Upon establishing milling and sintering processes, tapes were prepared for property evaluation. The dielectric constant (9-10) and loss (~ 0.001) are relatively flat across the frequency range until ionic resonances occur in the far infrared. The temperature coefficient of dielectric constant was ~ 120 ppm/ $^{\circ}\text{C}$ at 1 MHz measured from -55° to $+125^{\circ}\text{C}$. Average resistivity was 10^{15} ohm-cm. Thermal conductivity for sintered laminates of SECAR 71 was ~ 3 W/m-K. Flexural strengths were measured with 3-point bend (~ 100 MPa) and related to microstructural observations.

Tapes were cast with SECAR 71 cement and 30 vol.% hollow silica glass microspheres that had been sieved to $-32\text{ }\mu\text{m}$. The sintered laminates follow a Maxwell's dielectric mixing of discrete porosity. Dielectric constant was lowered from ~ 10 to ~ 7 without an increase in dielectric losses (0.001). Flexural strengths (up to 230 MPa) of the sintered laminates were remarkably high for a material containing at least 30 vol.% porosity. It is suggested that the pores are acting as "crack arrestors."

An exploratory study was undertaken to evaluate the effect of Nb_2O_5 additions on lowering the dielectric losses. Varying quantities of Nb_2O_5 were added to SECAR 71 cement during milling and sintered into disks. Q values at 1 MHz and dissipation factor in the microwave region for cements with Nb_2O_5 additions were approximately an order of magnitude lower (0.0001) than those cements sintered without Nb_2O_5 (0.0005-0.001).

APPENDIX 4

The Pennsylvania State University

The Graduate School

Electrical Conductivity and Dielectric Studies
of Hydraulic Cements

A Thesis in

Solid State Science

by


Marianela Perez Pena

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 1986

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Marianela Perez Pena

ABSTRACT

Electrical properties of portland cements and other non-portland cementitious materials have been studied at two different stages of hydration. These properties have been found to be highly influenced by processing parameters. The following relationships have been observed:

Higher water/cement (w/c) ratio (0.5 compared to 0.4) resulted in an increase of the relative permittivity and electrical conductivity measured during the first hours after mixing the cement powder with water. The relative permittivity values were close to 10^7 . This abnormal high value was attributed to electrode polarization.

Higher electrical conductivity and relative permittivity values were obtained for cement pastes with higher alkali ion concentration.

The phenomena giving rise to changes in electrical conductivity have been related to the heat evolved during the first 20 hours of hydration.

Cations of inorganic admixtures (chlorides and hydroxides) were found to increase maximum peak of electrical conductivity and relative permittivity upon hydrolysis in the order: $\text{Ca}^{++} > \text{Mg}^{++} > \text{Sr}^{++}$ and $\text{K}^+ \approx \text{Na}^+ > \text{Li}^+$.

Dielectric properties of pressed hardened materials cured over water for 1 day with w/c = 0.20 and heat treated to 500°C prepared with type I, type III, and a special microfine calcium silicate (MC500)

cement have been compared as a function of temperature and frequency.

The relative permittivity for type I hardened materials at 30°C was found to range from 12.5 to 9.4 at frequencies from 1 KHz to 2 MHz.

The loss $\tan \delta$ (dissipation factor) was found to range from 0.122 to

0.14 at the same temperature and frequencies. The relative permittivity and dissipation factors for type III hardened materials were found to range from 17.8 to 13.0 and from 0.035 to 0.071, respectively, under the same conditions. The relative permittivity and dissipation factor for MC500 hardened materials were determined to range from 7.6 to 6.9 and from 0.033 to 0.002, respectively.

The activation energies determined from Arrhenius plots for the relaxation mechanism operating in these materials were found to correspond to 0.33, 0.30, and 0.46 eV for type I, type III, and MC500 densified hardened materials, respectively.

Cement/polymer composites have been prepared using 1.76 wt.% methyl cellulose polymer and a w/c ratio = 0.17. Lower dielectric permittivities have been measured for the composites cured in polyethylene bags as compared to those cured over water. The relative permittivity and loss factor measured for the later ones ranged from 7.5 to 7.3 and from 0.01 to 0.005, respectively, at frequencies from 10 KHz to 1 MHz, while for the materials cured in polyethylene bags the range in values was from 5.6 to 5.4 and from 0.007 to 0.004.

The heat-treated hardened MC500 cement base materials containing 60 vol.% of silica microspheres were found to have the lowest relative permittivity when compared to other materials prepared in this study. The relative permittivity and loss factor of these materials ranged from 5.4 to 5.1 and from 0.035 to 0.012.

The intrinsic relaxation times obtained for hardened materials with type I and type II portland cements were 2.0×10^{-9} and 1.28×10^{-11} seconds, while for materials prepared with MC500 microfine cement the time was 2.27×10^{-12} seconds.

APPENDIX 5

The Pennsylvania State University

The Graduate School

Dielectric Properties of Porous Glass in the Microwave Region

A Thesis in
Ceramic Science

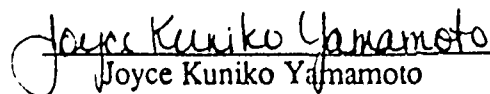
by
Joyce Kuniko Yamamoto

Submitted in Partial Fulfillment
of the Requirements
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Master of Science

December 1986

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Joyce Kuniko Yamamoto

ABSTRACT

The need for low dielectric constant, low-loss substrate materials for faster microwave signal transmission times has increased with the introduction of GaAs integrated circuits. Since the dielectric constant directly influences the operating speeds of these circuits, it has become a major limitation on the potential performance of these integrated circuits. In this study glass was chosen because it commonly possesses a low dielectric constant, and air was introduced as a second phase in the form of interconnected porosity. The microwave dielectric properties of Porous Vycor, manufactured by and registered trademark of Corning, was investigated as a function of thermal and chemical treatments. Porous Vycor is a phase-separated borosilicate glass leached to produce a highly porous silica skeleton. The Porous Vycor was treated in different hydrofluoric acid concentrations and leaching times and heated up to 1100°C in flowing oxygen. The microwave dielectric properties were measured using four resonant cavities, at 2.5 GHz, 3.0 GHz, 5.5 GHz, and 11.4 GHz. A minimum room temperature dielectric constant of 2.7 and loss of 0.001 were measured on samples heated to 800°C, which degraded with increasing exposure to the atmosphere. At higher temperatures the dielectric constant increased and the loss continued to slowly decrease, which was attributed to the densification process. There was little change in the dielectric constant with increasing frequency. No correlation could be made to the effect of the acid treatments on the dielectric behavior. Although additional work is needed to apply Porous Vycor to other packaging requirements, the dielectric properties of Porous Vycor has shown that it does have the potential to be considered as a candidate substrate material for high speed GaAs interconnect systems.

APPENDIX 6

The Pennsylvania State University
The Graduate School

Ultra-Low Permittivity Porous Silica Thick Films for GaAs IC Packaging

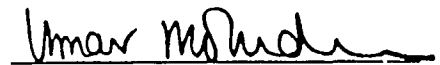
A Thesis in
Solid State Science
by

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December 1987

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Umar Mohideen

ABSTRACT

Evolving very high speed and very large scale integrated circuits along with the emerging complex GaAs integrated circuits demand radical changes in the device packaging technology, if one is to exploit their characteristics of very high switching speeds in digital computers. More attention needs to be focused on packaging material properties, process technology and interconnect design. The present trend in packaging is the multilayer micro-stripline configuration using glass bonded alumina (relative permittivity = 9.5) as the dielectric between the reference planes. With the expected increase in the circuit density of IC's and the sharp decrease in the signal rise time new dielectrics with a relative permittivity less than 3.0 are needed if one is to stay within the allowed limits of signal to noise ratio and propagation delay. .

This thesis describes a method to create a dielectric material with a relative permittivity in the range 2.4-2.8 and a loss tangent less than 0.01. These ceramic thick films are about 1 to 10 microns thick. They are made from a gel-like film formed from mixing a silica sol with different molecular weights of polymers like polyvinyl alcohol. They are easily compatible with the present technology of using glass bonded alumina substrates, while at the same time getting rid of all the disadvantages of using alumina in microelectronic packaging. They also can be processed at temperatures as low as 650°C thereby allowing for the use of low resistivity conductors like copper instead of the high resistivity refractory metal conductors now being used.

APPENDIX 7

The Pennsylvania State University

The Graduate School

THE USE OF SYNTHETIC ORGANIC TEMPLATES IN THE
PREPARATION OF TAILORED CERAMIC MICROSTRUCTURES

A Thesis in

Solid State Science

by

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ABSTRACT

This thesis demonstrates the formation of controlled microstructure silica templates from synthetic organic templates. The materials were evaluated as low permittivity substrates on the basis of dielectric properties and thermal expansion behavior. The porous silica membranes were fabricated via lamination, vacuum impregnation, thermolysis for selective removal of the organic template, and encapsulation in a polymer matrix. In these substrates, relatively nondispersive and temperature independent dielectric properties were obtained, with a dielectric constant less than three and losses less than 0.005. Thermal expansion coefficients were greater than the predicted values due to interaction between the polymer and silica. Although these properties are encouraging, other material properties need to be explored before the silica membranes can be considered for application. The technology described is not limited to silica; other sol compositions are suited to the process. In addition, other sol-template combinations should be explored for tailored microstructure composite materials.